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CHEMISTRY

Vol. XXIII

No. 2

February 2014

Corporate Office:

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he number of students taking science subjects is getting drastically reduced. This could affect our programs for technological advance of the nation.

We need scientists, working in basic sciences, medicine and computer technology, taking to fundamental and applied research in increasing numbers. We have made magnificent advances in almost every branch of science. We are in the closed group of nuclear science, computer technology and our achievements in the rocket technology are second to none. The achievements reached by our famous laboratories and research establishments should have fired not only the rockets but also the imagination of our students to be part of groups that are working on the frontiers of science.

Whatever be the cost of boosting science studies, the government has to take the problem by the horns. Barely within a month of the success of the launching the satellite to the Mars, now we have another great news from our rocket scientists at Vikram Sarabhai Space Centre, Liquid Propulsion Systems Centre and ISRO. Under the same leadership of ISRO, they have successfully launched GSLV D-5 rocket to put the GSAT-14 satellite in its orhit

The success of our rocket and satellite program, like our atomic energy program is something special. Both were in the teeth of opposition by U.S.A., Canada and other allies. Both the programs are successful, thanks to the moral and material help of U.S.S.R. (earlier), and now Russia. We congratulate the success of ISRO and other establishments. This is the true spirit of Gandhian self-reliance-Self-Reliance at all costs.

> Anil Ahlawat Editor

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT.

The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 7

JEE MAIN/PMTs

- To 500 cm³ of water 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression of freezing point? [Given: K_f = 1.86 K kg/mol and density of water = 0.997 g/cm³]
 - (a) 0.35 K (c) 0.75 K
- (b) 0.25 K (d) 0.23 K
- p-Cresol reacts with chloroform in alkaline medium to give the compound X which adds hydrogen cyanide to form the compound Y. Y on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

- 3. In context with the industrial preparation of hydrogen from water gas (CO + H₂), which of the following is the correct statement?
 - (a) CO is oxidised to CO₂ with steam in the presence of a catalyst followed by absorption of CO₂ in alkali.
 - (b) CO and H₂ are fractionally separated using differences in their densities.
 - (c) CO is removed by absorption in aqueous Cu₂Cl₂ solution.
 - (d) H₂ is removed through occlusion with Pd.

Solution Senders of Chemistry Musing

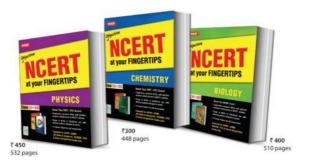
SET 6

- 1. Aravinda Krishnan R., Kollam (Kerala)
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- 4. A solution which is 10^{-3} M each in Mn^{2+} , Fe^{2+} , Zn^{2+} and Hg^{2+} is treated with 10^{-6} M sulphide ion. If K_{sn} of MnS, FeS, ZnS and HgS are 10⁻¹⁵, 10⁻²³, 10⁻²⁰ and 10⁻⁵⁴ respectively, which one will precipitate first?
 - (a) FeS
- (b) MnS
- (c) HgS
- (d) ZnS
- 5. The root mean square velocity of hydrogen is $\sqrt{7}$ times the root mean square velocity of nitrogen. If T is temperature of the gas then
 - (a) $T(H_2) = T(N_2)$
 - (b) $T(H_2) > T(N_2)$
 - (c) $T(H_2) < T(N_2)$
 - (d) $T(H_2) = \sqrt{7} T(N_2)$

JEE ADVANCED

- 6. An organic compound P is optically active with molecular formula C4H8O3. P on heating with conc. H₃PO₄ gives compound Q having molecular formula C4H6O2. Dilute chromic acid oxidises P to R(C4H6O3) which on heating with soda lime is converted into S(C3H6O). R and S both give iodoform test. Q decolourises alkaline KMnO4 in cold and gives acetic acid and oxalic acid on heating with it. P and S respectively are
 - (a) CH₃CH(OH)CH₂COOH, CH₃COCH₃
 - (b) CH2COCH2, CH2CH(OH)CH2COOH
 - (c) CH3CH=CHCOOH, CH3COCH3COOH (d) CH2CH(OH)CH2COOH, CH2COCH2COOH

COMPREHENSION

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite (CuSO₄.5H₂O), atacamite [Cu₂Cl(OH)₂], cuprite (Cu2O), copper glance (Cu2S) and malachite [Cu2CO3(OH)2]. However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

- 7. Partial roasting of chalcopyrite produces
 - (a) Cu₂S and FeO
 - (b) Cu₂O and FeO
 - (c) CuS and Fe₂O₂
 - (d) Cu₂O and Fe₂O₃
- 8. In self-reduction, the reducing species is
 - (a) S (c) S2-
- (d) SO₂

(b) O2-

INTEGER VALUE

- 9. An electron is moving with kinetic energy of 4.55×10^{-25} J. Its wavelength (in 10^{-7} m) is [Given: mass of an electron = 9.1×10^{-31} kg and $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$
 - 10. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C4H6 is

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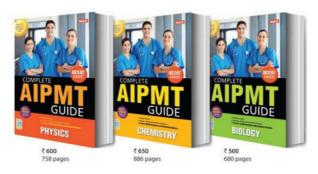
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Practice Paper 2014



Exam on 6th April

- 1. The correct order of first ionisation potential among the following elements Be, B, C, N, O is
 - (a) B < Be < C < O < N (b) B < Be < C < N < O
 - (c) Be < B < C < N < O (d) Be < B < C < O < N
- 2. Which of the following reactions will not give a primary amine?
 - (a) $CH_3CH_2CONH_2 \xrightarrow{Br_2/NaOH}$
 - (b) $CH_3CH_2NC \xrightarrow{LiAlH_4/ether}$
 - (c) CH₃CH₂CN LiAlH₄/ether
 - (d) CH₃CH₂CONH₂ LiAlH₄/ether
- 3. A dust particle having mass equal to 10⁻¹¹ g, diameter 10-4 cm and velocity 10-4 cm s-1. If the error in measurement of velocity is 0.1% then the uncertainty in its position is
 - (a) 5.57×10^{-10} cm (b) 5.27×10^{-6} m

 - (c) 5.27×10^{-6} cm (d) 5.27×10^{-10} m
- 4. In a compound C, H and N are present in 9:1:3.5 by weight. If molecular weight of the compound is 108, the molecular formula of compound is
 - (a) C₂H₆N₂
- (b) C₂H₄N
- (c) C₆H₈N₂
- (d) C₉H₁₂N₃
- 5. An organic compound P has 76.6% C and 6.38% H. Its vapour density is 47. It gives a characteristic colour with ag. FeCl₃. P when treated with CO2 and NaOH at 140°C under pressure gives Q which on acidification gives R. R reacts with acetyl chloride to give S, which is

- Which of the following pairs of species are isoelectronic?
 - (a) NO3, CIO2
- (b) CO₃², NO₃
- (c) CO₃²⁻, SO₃
- (d) Both (b) and (c)
- 7. $X + Y \stackrel{CN^-}{\longleftrightarrow} CH_3 CH = CH CH_2CI \stackrel{CN^-}{\longleftrightarrow} X$

The types of the reactions (i) and (ii) are respectively

- (a) S_N2, S_N1 (c) S_N1, S_N2
- (b) E1, E2 (d) E2, E1
- 8. The solubility of sulphates in water down the IIA group follows the order Be > Mg > Ca > Sr > Ba.
 - This is due to
 - (a) increase in melting point
 - (b) increasing molecular mass
 - (c) decreasing lattice energy
 - (d) high heat of solvation of smaller ions.
- The oxidation number of S in Caro's acid (H₂SO₅) is
 - (a) +5
- (b) +3
- (c) + 2
- (d) + 6
- 10. The ease of dehydration in the following compounds is

- (a) I > III > IV > II
- (b) II>I>III>IV
- (c) IV > I > III > II
- (d) III > I > II > IV
- From 200 mg of CO₂, 10²¹ molecules are removed. How many moles of CO2 are left?
 - (a) 2.88×10^{-5}
- (b) 2.88 × 10⁻³
- (c) 0.127
- (d) 0.075

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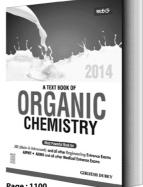
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- 12. 127 mL of a certain gas X diffuse in the same time as 100 mL of chlorine under the same conditions. The gas X is
 - (a) SO₂
 - (c) CO₂
- (b) CH₄ (d) H₂S
- Identify the incorrect statement.
 - (a) Ozone is present in the upper atmosphere, where it is formed by the action of UV radiations on dioxygen.
 - (b) Ozone absorbs infrared radiations and protects earth from its harmful effects.
 - (c) Ozone layer in the stratosphere is deflected by nitric oxide, atomic oxygen and reactive hydroxyl radicals.
 - (d) All the statements are correct.
- 14. Identify 'Z' in the sequence:

$$C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl} X \xrightarrow{CuCN} Y \xrightarrow{H^{\dagger}/H_2O} Z$$

- (a) C₆H₅CN
- (b) C₆H₅CONH₂
- (c) C₆H₅COOH (d) C₆H₅CH₂NH₂
- 15. When MnO2 is fused with KOH, a coloured compound is formed, the product and its colour is
 - (a) K₂MnO₄, purple-green
 - (b) KMnO₄, purple
 - (c) Mn₂O₃, brown
 - (d) Mn₃O₄, black.
- The correct decreasing order of the O-O bond strength present in O2, KO2 and O2[AsF4] is

 - (a) $O_2 > O_2^+ > O_2^-$ (b) $O_2^+ > O_2^- > O_2$

 - (c) $O_2^- > O_2 > O_2^+$ (d) $O_2^+ > O_2 > O_2^-$
- 17. Which of the following is a correct decreasing order of boiling points of the given isomeric compounds? Ethyldimethylamine (I), N-Butylamine (II), Diethylamine (III)
 - (a) II > III > I (b) I > II > III
 - (c) III > II > I
- (d) III > I > II
- The values of x, y and z in the following reaction are respectively

$$xMnO_4^- + yH^+ + zNO_2^- \longrightarrow$$

$$xMn^{2+} + \frac{y}{2}H_2O + zNO_3^{-}$$

- (a) 6, 2, 5
- (b) 5, 2, 6
- (c) 2, 5, 6
- (d) 2, 6, 5
- 19. The hybridisation of atomic orbitals of the transition metals in the following complexes are respectively

$${[Fe(H_2O)_6]^{3^+}, [Co(NH_3)_6]^{3^+}, [Ni(CN)_4]^{2^-}, [Ni(CO)_4]}$$

- (a) d^2sp^3 , sp^3d^2 , dsp^2 , sp^3
- (b) sp³d², d²sp³, sp³, dsp²
- (c) sv^3d^2 , d^2sv^3 , dsv^2 , sv^3
- (d) d^2sv^3 , sv^3d^2 , sv^3 , dsv^2
- 20. In the reaction HCN + $H_2O \rightleftharpoons H_3O^+ + CN^-$, the conjugate acid-base pair is
 - (a) HCN, H₃O⁺
 - (b) H₂O, CN⁻
 - (c) CN⁻, H₃O⁺
- (d) HCN, CN
- 21. The rate constant of a reaction is 1.5 × 10⁷ s⁻¹ at 50°C and 4.5 × 10⁷ s⁻¹ at 100°C. The Arrhenius parameter A is
 - (a) $5.42 \times 10^8 \text{ s}^{-1}$
- (b) $5.42 \times 10^6 \text{ s}^{-1}$
- (c) $5.42 \times 10^{12} \text{ s}^{-1}$
- (d) $5.42 \times 10^{10} \text{ s}^{-1}$
- 22. The element with the highest ionisation energy among the following is
 - (a) [He] $2s^22p^1$ (c) [Hel 2s²2v³

(c) AlCl₃

- (b) [He] $2s^22p^2$ (d) [He] 2s²2v⁴
- 23. As₂S₃ is negatively charged sol. Capacity to precipitate it is highest in
 - (a) K₂SO₄ (b) Na₃PO₄
 - (d) CaCl₂
- 24. The order of stability of the following carbocations

- (a) I > II > III > IV
- (b) III > II > IV > I(c) IV > III > II > I (d) III > II > IV
- 25. Identify the correct statement.
 - (a) Bond order of N2 is more than that of N2 whereas in O2 it is less than O2.
 - (b) Bond order of N2+ is equal to that of N2 whereas in O2 it is more than O2.
 - (c) Bond order of N2+ is less than that of N_2 whereas in O_2^+ it is more than O_2 .
 - (d) Bond order of N2+ is less than that of N_2 whereas in O_2^+ it is equal to that of O_2 .
- 26. A hydrocarbon P of the formula C7H12 on ozonolysis gives a compound Q which undergoes aldol condensation giving 1-acetylcyclopentene. The compound P is

- 27. Amongst TiF₆², CoF₆³, Cu₂Cl₂ and NiCl₄² (At. nos. of Ti = 22, Co = 27, Cu = 29, Ni = 28), The colourless species are
 - (a) CoF₂³ and NiCl₂² (b) TiF₂² and CoF₂³
 - (c) Cu₂Cl₂ and NiCl₄²⁻ (d) TiF₆²⁻ and Cu₂Cl₂
- 28. A sample of wustite contains one Fe (III) for every three Fe (II). The amount of oxygen atoms (in moles) is

- 29. The bond enthalpy of H_{2(e)} is 436 kJ mol⁻¹ and that of N_{2(g)} is 941.3 kJ mol⁻¹. Calculate the average bond enthalpy of an N-H bond in ammonia if $\Delta H_{f}^{\circ}(NH_{3}) = -46.0 \text{ kJ mol}^{-1}$.
 - (a) 443.67 kJ mol⁻¹ (b) 474.33 kJ mol⁻¹
 - (d) 244.88 kJ mol⁻¹ (c) 390.2 kJ mol-1
- 30. Which of the following will not reduce Tollen's reagent?

- (a) (X) only
- (b) (Y) only
- (c) Both (X) and (Y)
- (d) Neither (X) nor (Y)

1. (a): Due to the extra stability of half-filled v-orbitals of N, its first ionisation potential is higher than those of O and C. Further because of higher nuclear charge, first ionisation potential of C is higher than that of Be and B. Amongst Be and B, the first ionisation potential of Be is higher than that of B because in case of Be, an electron is to be removed from 2s2 orbital while in case of B, an electron is to removed from 2p1 orbital. Thus, the overall order is B < Be < C < O < N.

- (c): Applying uncertainty principle,

$$\Delta v = \frac{10^{-4} \times 0.1}{100} = 1 \times 10^{-7} \,\mathrm{cm \ s}^{-1}$$

As
$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$\Delta x = \frac{6.625 \times 10^{-27}}{4 \times 3.14 \times 10^{-11} \times 1 \times 10^{-7}} = 5.27 \times 10^{-10} \text{ cm}$$

Uncertainty in position as compared to particle

size =
$$\frac{\Delta x}{\text{diameter}}$$

= $\frac{5.27 \times 10^{-10}}{10^{-4}}$ = 5.27 × 10⁻⁶ cm

4. (c): Wt. of C: Wt. of H: Wt. of N 9 : 1 :

Moles of 0	C :	Moles of H	:	Moles of l
9		1	:	3.5
12	•	1	•	14
0.75	:	1	:	0.25

Empirical formula is C3H4N. Empirical formula mass = $3 \times 12 + 4 \times 1 + 14 = 54$ Molecular mass = 108

$$n = \frac{108}{54} = 2$$

Molecular formula = (Empirical formula), = C6H8N2

5. (d): To determine empirical formula from data:

Element	%	Relative no. of atoms	Simple ratio
С	76.6	$\frac{76.6}{12} = 6.38$	6
Н	6.38	$\frac{6.38}{1} = 6.38$	6
0	17.02	$\frac{17.02}{16} = 1.06$	1

- Empirical formula $(P) = C_6H_6O$ Empirical formula weight = 94 Molecular weight = $2 \times VD = 2 \times 47 = 94$
- Molecular formula of P is C_6H_6O . Since P gives colour with aq. FeCl3 it has a

Compound P should be C_6H_5OH (phenol).

phenolic group.

$$(P) \xrightarrow{OH} (P) \xrightarrow{NaOH + CO_2} (Q) \xrightarrow{OH} (HOH) \xrightarrow{H^t} (P) \xrightarrow{(P)} (COONa \xrightarrow{OH} (P) \xrightarrow{COOH} (R) \xrightarrow{(R)} (P) \xrightarrow{COOH} (R) \xrightarrow{Aspirin (pain killer)} (Salicylic acid)$$

(b): Number of electrons in NO₃ $= 7 + (3 \times 8) + 1 = 32$ Number of electrons in $CO_3^{2-} = 6 + (3 \times 8) + 2 = 32$ Number of electrons in $ClO_2^- = 17 + (2 \times 8) + 1 = 34$

Number of electrons in $SO_3 = 16 + (3 \times 8) = 40$ Therefore, NO₃ and CO₃² are isoelectronic.

7. (c):
$$CN^{-} CH_{3}-CH=CH-CH_{2}CI \frac{CN^{-}}{(ij) S_{N}^{2}} Slow$$

$$CH_{3}-CH=CH^{-}CH_{2} CH_{3}-CH=CH^{-}CH_{2} CH_{3}-CH=CH^{-}CH_{2} CH_{3}-CH=CH^{-}CH_{2} CH_{3}-CH=CH^{-}CH_{2} CH_{3}-CH^{-}CH^{-}CH^{-}CH_{2} CH_{3}-CH^{-}CH$$

- 8. (d): The solubilities of BeSO4 and MgSO4 are highest due to high energy of solvation of smaller Be2+ and Mg2+ ions. The value of solubility product decreases which explains decrease in solubility on moving down the group.

Two oxygen atoms are in peroxo linkage i.e., oxidation number = -1

$$3 (-2) + 2(-1) + x + 2(+1) = 0$$

$$-8 + x + 2 = 0$$

$$x = +6$$

- (a): Allylic carbocation is more stable and C—H bond is easily broken compared to C-D bond. Hence, the order is I > III > IV > II.
- 11. (b): Gram-molecular mass of CO₂ = 44 g Mass of 1021 molecules of CO2

$$= \frac{44}{6.023 \times 10^{23}} \times 10^{21} = 0.073 \text{ g}$$

Mass of CO_2 left = (0.2 - 0.073) = 0.127 g Number of moles of CO_2 left = $\frac{0.127}{44}$ = 2.88×10^{-3}

(c): If t is the time taken for diffusion of each gas. then by Graham's law of diffusion,

$$\frac{r_X}{r_{\text{Cl}_2}} = \frac{127 / t}{100 / t} = \sqrt{\frac{M_{\text{Cl}_2}}{M_X}} = \sqrt{\frac{71}{M_X}}$$

or
$$\frac{71}{M_X} = \left(\frac{127}{100}\right)^2$$
 or $M_X = 44 \text{ u}$

Hence, the gas X is CO2 having molecular mass 44 11.

- 13. (b): Ozone absorbs ultraviolet radiations and protects earth from its harmful effects.
- 14. (c): $C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl} C_6H_5N_2^*Cl^{-\frac{CuCN}{(\chi)}}$ $C_6H_5COOH \leftarrow \frac{H^+/H_2O}{Boil} C_6H_5CN$
- 15. (a): In alkaline medium, the stable oxidation state of Mn is +6. Hence, MnO2 is oxidised to K2MnO4 (purple-green) by atmospheric oxygen on fusion with KOH.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

16. (d): Since bond strength ∞ bond order, so we calculate the bond order in the given species. $O_2 : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$

$$\therefore B.O. = \frac{10-6}{2} = 2$$

 O_{2}^{-} (in KO₂): $\sigma_{1}^{2} \sigma_{1}^{2} \sigma_{2}^{2} \sigma_{2}^{2} \sigma_{3}^{2} \sigma_{2}^{2} \sigma_{2}^{2}$

$$\therefore$$
 B.O. = $\frac{10-7}{2}$ = 1.5

 O_2^+ (in $O_2[AsF_4]$): $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p^2 \pi 2p^2$

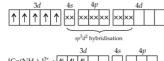
$$\therefore$$
 B.O. = $\frac{10-5}{2}$ = 2.5

The B.O. of three species follows the order

 $O_2^+ > O_2 > O_2^-$ Bond strength in decreasing order is

 $O_2^+ > O_2 > O_2^-$

- 17. (a): 1° and 2° amines, unlike 3° amines form intermolecular H-bonding. 1° amine with two H's available for H-bonding has a higher boiling point than 2° amine
- 18. (d): $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$
- 19. (c): [Fe(H₂O)₆]³⁺:



$$\frac{1}{d^2 s p^3 \text{ hybridisation}} = \frac{1}{|\mathcal{V}|} \frac{1}{|\mathcal{V}|} \frac{1}{|\mathcal{V}|} \frac{|\mathcal{V}|}{|\mathcal{V}|} \frac{|\mathcal{V}$$

$$[Ni(CN)_4]^{2-}: \boxed{1 \hspace{-0.1cm} |\hspace{-0.1cm} 1 \hspace{-0.1cm} |\hspace{-0.1cm} 1$$

[Ni(CO)₄]:
$$3d$$
 $4s$ $4v$ $xx xx xx$

- 20. (d): HCN + H₂O ⇒ H₃O⁺ Conjugate acid Conjugate base
- 21. (d): Using the relation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$
, we get

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.314} \left[\frac{373 - 323}{323 \times 373} \right]$$

or
$$\log 3 = \frac{E_a \times 50}{2.303 \times 8.314 \times 323 \times 373}$$

or $E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$ Again,

$$\begin{aligned} \log_{10} k &= \log_{10} A - \frac{E_a}{2.303 \, RT} \\ \log_{10} (4.5 \times 10^7) &= \log_{10} A - \frac{2.2 \times 10^4}{2.303 \times 8.314 \times 373} \end{aligned}$$

$$A = 5.42 \times 10^{10} \text{ s}^{-1}$$

- 22. (c): The element with half-filled electronic configuration is most stable and therefore shows highest ionisation energy.
- 23. (c): AlCl3 has highest capacity to precipitate As₂S₃ sol because AlCl₃ produces Al³⁺ ion which has the maximum valency among the all.
- 24. (b): Electron releasing group stabilises while electron withdrawing group destabilises the benzylium carbocation.
- 25. (c): N₂⁺ is formed by the removal of an electron from the bonding $\sigma 2p_z$ molecular orbital which causes the reduction in the bond order in N2, it becomes 2.5 in N_2^+ from 3 in N_2 .

$$N_2^+$$
: $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^1$

Bond order of
$$N_2^+ = \frac{N_b - N_a}{2} = \frac{9 - 4}{2} = 2.5$$

But O2 is formed by the removal of an electron from the antibonding (π^*2p_y) or (π^*2p_y) molecular orbital which causes an increase in the bond order in O₂⁺, it becomes 2.5 from 2 in O₂.

$$O_2^+$$
: $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2$

.. Bond order of
$$O_2^+ = \frac{N_b - N_a}{2} = \frac{10 - 5}{2} = 2.5$$

26. (a):

$$\begin{array}{c} \text{CH}_{3} \\ \text{Ozonolysis} \\ \text{1-Methylcyclohexene} \\ \text{(P)} \\ \text{H}_{2} \\ \text{C} \\ \text{CH}_{3} \\ \text{CH}_{4} \\ \text{Sation} \\ \text{H}_{2} \\ \text{C} \\ \text{CH}_{3} \\ \text{Condensition} \\ \text{H}_{2} \\ \text{C} \\ \text{CH}_{3} \\ \text{Condensition} \\ \text{CO} \\ \text{Condensition} \\ \text{CO} \\ \text{Condensition} \\ \text{CO} \\ \text{C} \\ \text{C$$

27. (d): Oxidation state of

Ti in
$$TiF_6^{2-} = +4 i.e. Ti^{4+} \longrightarrow 3d^0$$

Co in $CoF_6^{3-} = +3 i.e. Co^{3+} \longrightarrow 3d^6$

Ni in NiCl₄²⁻ = + 2 *i.e.* Ni²⁺
$$\longrightarrow$$
 3d⁸

Cu in
$$Cu_2Cl_2 + 1$$
 i.e. $Cu^+ \longrightarrow 3d^{10}$

Colour of salts is a property of partially filled d-orbitals. Since TiF62- has completely empty and Cu₂Cl₂ has completely filled d-subshells, hence these are colourless salts.

28. (d): Let there be 1 mol of iron atom.

Amount of Fe (III) =
$$\left(\frac{1}{4}\right)$$
 mol;

Amount of Fe (II) =
$$\left(\frac{3}{4}\right)$$
 mol

Total moles of positive charge

$$=\left(\frac{1}{4}\right)(+3)+\left(\frac{3}{4}\right)(+2)=\left(\frac{9}{4}\right)$$
mol

Let x be the amount of oxygen atoms. Total moles of negative charge = 2x

To satisfy electrical neutrality,

Total moles of positive charge = Total moles of negative charge

$$\frac{9}{4}$$
 mol = $2x \implies x = \frac{9}{8}$ mol

29. (c): Given

$$\begin{array}{lll} N_{2(g)} & \rightarrow 2N_{(g)} \; ; \; \Delta H^{\circ} = 941.3 \; \text{kJ mol}^{-1} & ...(i) \\ H_{2(g)} & \rightarrow 2H_{(g)} \; ; \; \Delta H^{\circ} = 436.0 \; \text{kJ mol}^{-1} & ...(ii) \\ \frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} & \longrightarrow NH_{3(g)} ; \Delta H^{\circ} = -46.0 \; \text{kJ mol}^{-1} & ...(iii) \end{array}$$

Multiply eqn. (i) by $\frac{1}{2}$ and (ii) by $\frac{3}{2}$ then add, we get

$$\frac{1}{2}\,N_{2(g)} + \frac{3}{2}\,H_{2(g)} \longrightarrow N_{(g)} + 3H_{(g)}\,;$$

$$\Delta H^{\circ} = 941.3 \times \frac{1}{2} + 436.0 \times \frac{3}{2}$$
 ...(iv)

= 470.65 + 654 = 1124.65 kJ mol⁻¹

Now subtract eqn (iii) from eqn. (iv), we get $NH_3 \longrightarrow N_{(g)} + 3H_{(g)}$; ...(v)

 ΔH° = 1124.65 – (-46.0) kJ mol⁻¹ = 1170.65 kJ mol⁻¹ Since there are three N-H bonds in NH₃, the average bond enthalpy is obtained by dividing the value of ΔH° of ean. (v) by 3.

Hence,
$$\Delta H_{N-H} = \frac{1170.65}{3} = 390.2 \text{ kJ mol}^{-1}$$

30. (a): Structure (X) is of sucrose, a disaccharide which is a non-reducing sugar. Thus, it does not react with Tollen's reagent whereas (Y) is maltose, a reducing sugar.

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Questions for Medical/ Engineering Entrance Exams

Biomolecules | Polymers | Chemistry in Everyday Life

- 1. Lactose is a disaccharide of
 - (a) α-D-galactose and α-D-glucose
 - (b) β-D-galactose and β-D-glucose
 - (c) α-D-galactose and β-D-glucose
 - (d) β-D-galactose and α-D-glucose.
- 2. Which of the following is a biodegradable polymer?
 - (a) Nylon-6, 10
- (b) Buna-N
- (c) PHBV
- (d) Teflon
- Identify the correct statement.
 - (a) Amylose is insoluble in water while amylopectin is water soluble.
 - (b) Both amylose and amylopectin are insoluble in water.
 - (c) Both amylose and amylopectin are soluble in
 - (d) Amylose is water soluble while amylopectin is insoluble in water.
- 4. Which of the following is not used as an artificial sweetening agent?
 - (a) Aspartame (c) Alitame
- (b) Saccharin
- (d) Novestrol
- 5. Which of the following statements indicates the cyclic structure of glucose?
 - (a) Glucose gets oxidised to gluconic acid on reaction with bromine water. (b) Glucose on heating with HI forms n-hexane.

 - (c) Glucose does not give 2, 4-DNP test.
 - (d) All of the above.

- 6. Which of the following is a synthetic rubber? (b) Natural rubber
 - (a) Teflon
- (c) Chloroprene (d) Neoprene
- 7. Scurvy is a disease caused by the deficiency of (a) vitamin D (b) vitamin C
 - (c) ascorbic acid
 - (d) both (b) and (c).
- 8. Which of the following is an incorrect statement?
 - (a) 0.2% solution of phenol is a disinfectant.
 - (b) 1% solution of phenol is an antiseptic.
 - (c) Penicillin G is a narrow spectrum antibiotic.
 - (d) Both (a) and (b).
- 9. Glycine
 - (a) exists as a zwitter ion
 - (b) shows optical activity
 - (c) contains two carboxyl groups
 - (d) contains two amino groups.
- 10. Which of the following is not an antidepressant drug?
 - (a) Iproniazid
- (b) Phenelzine
- (c) Meprobamate
- (d) Seldane
- 11. Mark the wrong statement about denaturation of
 - (a) The primary structure of the protein does not
 - (b) Globular proteins are converted into fibrous
 - (c) Fibrous proteins are converted into globular proteins.
 - (d) The biological activity of the protein is destroyed.

24. The tensile strength, elasticity and resistance to abrasion can be increased by a process called (a) diazotisation (b) vulcanization (c) isomerization (d) polymerization. 25. Which of the following is the basic amino acid? (a) Lysine (b) Glycine (c) Leucine (d) Alamine
26. Amylose is a long unbranched chain of α-D-(+)-glucose units held by glycosidic linkage.
(a) C1-C6 (b) C1-C4 (c) C2-C6 (d) C2-C4 27. Glyptal is the polymer of (a) ethylene glycol and terephthalic acid
(b) phenol and formaldehyde (c) 1,3-butadiene and acrylonitrile (d) ethylene glycol and phthalic acid. 28. Equanil is a/an
(a) artificial sweetener (b) tranquilizer (c) antihistamine (d) antifertility drug 29. Which of the following is addition homopolymer?
(a) Teflon (b) PVC (c) Polystyrene (d) All of the above. 30. Structurally a biodegradable detergent should contain a (a) normal alkyl chain (b) branched alkyl chain
(c) phenyl side chain (d) cyclohexyl side chain.
(a) aqueous solution of I ₂ (b) solution of I ₂ in aqueous KI (c) alcoholic solution of I ₂
(d) aqueous solution of KI. 32. Which of the following is thermosetting polymer? (a) Polythene (b) Nylon-6, 6 (c) Bakelite (d) Buna-S
33. Which of the following is not an antibiotic? (a) Chloramphenicol (b) Streptomycin
(c) Penicillin (d) Bithional 34. Among the following, natural polymer is (a) Proteins (b) Starch
(c) Buna-S (d) both (a) and (b). 35. Which of the following is not used to preserve food?
(a) Sodium benzoate (b) Salts of sorbic acid (c) Salts of propanoic acid (d) Glucose



HIGHER ORDER THINKING SKILLS QUESTIONS (HOTS)

- 36. Which of the following chemicals is used as pain killer?
 - (a) Phenyl acetate (b) Methyl acetate (c) Acetyl salicylic acid (d) Salicylic acid
- 37. 1, 3-Butadiene is one of the monomers of
 - (a) Buna-S
- (b) Buna-N
- (c) Natural rubber (d) both (a) and (b).
- 38. The given structure is

- (a) α-D-(+)-glucopyranose
- (b) β-D-(+)-glucopyranose
- (c) α-D-(+)-glucofuranose
- (d) β-D-(+)-glucofuranose.
- 39. Copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid gives
 - (a) PMMA (b) PVC
 - (c) PHBV
- (d) dacron.
- 40. Which of the following is a reducing sugar? (b) Maltose (a) Lactose
 - (c) Sucrose
- (d) Both (a) and (b)
- 41. Which among the following antibiotics is bacteriostatic?
 - (a) Penicillin
- (b) Ofloxacin
- (c) Aminoglycosiders (d) Erythromycin
- 42. Cross-linking is present in
 - (a) polythene (b) bakelite
 - (c) nylon-6
- (d) polyester.
- 43. Dettol consists of
 - (a) xylenol + terpineol (b) chloroxylenol + terpineol
 - (c) cresol + ethanol
 - (d) None of these.

Identify the correct statement.

- (a) Glycosidic linkage is between C-1 of galactose and C-4 of glucose.
- (b) Glycosidic linkage is between C-4 of galactose and C-1 of glucose.
- (c) Glycosidic linkage is between C-5 of galactose and C-2 of glucose.
- (d) Glycosidic linkage is between C-2 of galactose and C-5 of glucose.
- 45. Gammaxane is
 - (a) DDT
 - (b) hexachlorobenzene (HCB)
 - (c) benzene hexachloride (BHC)
 - (d) chloral.

SOLUTIONS

1. (b): H₂OH ČH₄OH HO ÓН OH B-D-Galactose β-D-Glucose

- 2. (c): PHBV is a biodegradable polymer as it undergoes bacterial degradation in the environment.
- 3. (d)
- (d): Novestrol is an antifertility drug.
- 5. (c)
- 6. (d)
- 7. (d): The chemical name of vitamin C is ascorbic acid. Its deficiency causes scurvy (bleeding gums).
- 8. (d): 0.2% solution of phenol is an antiseptic while its 1% solution is used as a disinfectant.
- 9. (a): Glycine (H2N-CH2-COOH) exists as a zwitter ion $(H_3N^+-CH_2-COO^-)$.
- 10. (d): Seldane is an antihistamine drug.
- 11. (c)
- 12. (b): It constitutes condensation polymer having ester linkages. 14. (c)
- 13. (b)

Bakelite

benzyl alcoho

- 16. (d) 17. (b)
- (b): Polymers having amide linkages are known as polyamides.

$$\begin{array}{ll} nNH_2-(CH_2)_6-NH_2+nHOOC-(CH_2)_4-COOH\\ Hexamethylenediamine & Adipic acid\\ & \text{amide linkage}\\ +NH-(CH_2)_6-\underbrace{NH-CO}_-(CH_2)_4-CO-\underbrace{J_n} \end{array}$$

19. (a):

 (c): Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups.

- 21. (d)
- (d): Dacron is a polymer of ethylene glycol and terephthalic acid.
- 23. (c): Weak bonds such as hydrogen bonds, van der Waals' forces are formed between enzyme and inhibitor.
- 24. (b): Vulcanization is a process in which natural rubber is treated with 3-5% sulphur. It introduces sulphur bridges between polymer chains thereby

- increasing its tensile strength, elasticity and resistance to abrasion.
- (a): In lysine, number of amino (-NH₂) groups is greater than number of carboxyl (-COOH) groups.

COOH
$$H_2N \xrightarrow{\hspace{1cm}} H$$

$$CH_2 \xrightarrow{\hspace{1cm}} (CH_2)_3 \xrightarrow{\hspace{1cm}} NH_2$$

28. (b)

- 26. (b) 27. (d)
- (d): Teflon, PVC and polystyrene are the examples of addition homopolymerisation as only single monomer undergoes addition reaction.
- (a): Biodegradable detergent should contain a normal alkyl chain.
- (c): 2-3% solution of iodine in alcohol-water mixture is known as tincture of iodine.
- **32. (c)**: Polythene is thermoplastic. Nylon-6, 6 is a fibre.

Bakelite is thermosetting polymer. Buna-S is an elastomer.

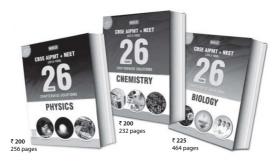
- (d): Bithional is used as an antiseptic in medicated soaps.
- 34. (d)
- 35. (d): Glucose cannot be used as food preservative because bacteria can utilise glucose and grow in food stuff and thereby contaminate it.
- 36. (c)
- **37.** (d): Buna-S is the copolymer of 1, 3-butadiene and styrene.

Buna-N is the copolymer of 1, 3-butadiene and acrylonitrile.

Natural rubber is the homopolymer of isoprene (2-methyl-1, 3-butadiene).

- 39. (c)
- (d): Both lactose and maltose are reducing sugars while sucrose is a non-reducing sugar.
- 41. (d) 42. (b) 43. (b)
- 44. (a) 45. (c)

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YQU ASKED WE ANSWERED

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The best questions and their solutions will be printed in this column each month.

Q1. What chemicals are used to detect and identify breast cancer?

- Suman, Delhi

Ans. Breath analysis, using the volatile organic compounds (VOC) biomarkers of breast cancer, and nanowire is an accurate and non-invasive diagnostic method. In this method, palladium, polypyrrole and zinc oxide nanowires, fabricated using electrochemical deposition method, perform quick response and high sensitivity to the four VOC biomarkers of breast cancer, including heptanal, 1-phenylethanone (acetophenone), isopropyl myristate and 2-propanol.

(Polypyrrole) Q2. Nowadays, thermometers contain which chemicals other than mercury?

- Pooja Verma, Saharanpur

Ans. The alcohol thermometer also called spirit thermometer is an alternative to the mercury thermometer, and functions in a similar way. But unlike mercury, the contents of an alcohol thermometer are less toxic and will evaporate away quickly. An organic liquid such as pure ethanol, toluene, kerosene or isoamyl acetate (isopentyl acetate) is filled in a glass bulb which is connected to a capillary

of the same glass and the end (Isoamyl acetate)

is sealed with an expansion bulb. The space above the liquid contains a mixture of nitrogen and the vapours of the liquid. Since the liquid is transparent, it is made more visible by the addition of a red or blue dye.

Q3. In countries where temperature is below 0°C, which chemicals are used to keep water in liquid state?

- Harsh Pandey, Varanasi

Ans. Antifreeze and de-icers are used for this purpose. An antifreeze is a chemical additive which lowers the freezing point of a water-based liquid. e.g., methanol (CH₂OH), ethylene glycol (CH₂OH)₂, propylene glycol (C₃H₈O₂), glycerol (C₃H₈O₃). Anti-icing is understood to be the application of chemicals that not only de-ice, but also remain on a surface and continue to delay the reformation of ice for a certain period of time, or prevent adhesion of ice to make mechanical removal easier. e.g., inorganic salts like NaCl, MgCl₂, CaCl₂, KCl and organic compounds such as calcium magnesium acetate, potassium acetate, HCOOK, HCOONa. CalfHCOOl₂.

Q4. Why should not we use mosquito coils at our home?

- Amit Sharma, Madhya Pradesh

Ans. Mosquito coils often contain BCME [bis-(chloromethyl) ether] which is a dangerous, lung-cancer causing chemical.

Q5. What is the chemistry behind disappearing inks?

- Rohit Bhatia, Hyderabad

Ans. Disappearing ink is also known as security ink. It is a mixture of thymolphthalein indicator, ethyl alcohol, sodium hydroxide, and water at pH 11. Thymolphthalein is a weak organic acid that behaves as an acid-base indicator in the pH range 9.3 (colourless) to 10.5 (blue). It exists in two different forms-an acid form HInd, which is colourless, and a corresponding conjugate base form Ind-, which is blue. When the blue ink is applied to paper, the blue colour quickly vanishes. The disappearance of the blue ink colour in air is due to the effect of CO2, which reacts with moisture in the air to form carbonic acid (H2CO3) - the pH change is enough to push the basic form of the indicator (Ind-) back to its colourless acidic form (HInd).

$$CO_2 + H_2O \Longrightarrow H_2CO_3$$

 $H_2CO_3 + Ind^- \Longrightarrow HCO_3^- + HInd$
Blue Colourless

RNFAST

Chemical Kinetics

- Chemical kinetics deals with
 - study of the rates of chemical reactions.
 - factors affecting the rates of the reactions.
 - mechanism by which the reactions proceed.

Classification of Reactions on the basis of Rates

- Very fast reactions: Some reactions such as ionic reactions occur very fast. For example, precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride.
- □ Very slow reactions : Some reactions are very slow. For example, rusting of iron in the presence of air and moisture
- Moderate reactions : Reactions which are neither very slow nor very fast but take place at moderate speeds. Reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed.

Rate of Reaction

- Rate = $\frac{\text{Moles of reactants used}}{\text{Time required for this change}} = \frac{x}{t}$
- Rate = $\frac{\text{Change in concentration}}{\text{Time taken for change}} = \frac{dx}{dt}$
- Its unit is mol L-1 s-1.
- For a reaction, $A \rightarrow B$, the rate may be expressed in two ways:

Rate =
$$\frac{\text{Decrease in concentration of } A}{\text{Time taken}}$$

= $-\frac{[A]_2 - [A]_1}{t_2 - t_1} = \frac{-\Delta[A]}{\Delta t}$
where $[A]_2$ and $[A]_1$ are molar concentration.

where $[A]_2$ and $[A]_1$ are molar concentrations of A at a time t_2 and t_1 respectively.

Rate =
$$\frac{\text{Increase in concentration of } B}{\text{Time taken}}$$

= $\frac{[B]_2 - [B]_1}{t_1 - t_1} = \frac{\Delta[B]}{\Delta t}$

where $[B]_2$ and $[B]_1$ are the molar concentrations of B at time t_2 and t_1 respectively.

Significance of -ve sign The concentration of reactants decreases during a reaction i.e., $\Delta[A] = [A]_2 - [A]_1 = -ve$.

Therefore, $\frac{\Delta[A]}{\Delta t}$ will be negative. But the rate

of reaction is always positive. So a (-) sign is put before $\frac{\Delta[A]}{\Delta t}$ so that $\frac{\Delta[A]}{\Delta t}$ is positive.

For the reaction,

$$2P + 3Q \longrightarrow 4R + 5S$$

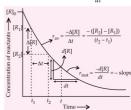
Rate =
$$\frac{-1}{2} \frac{d[P]}{dt} = \frac{-1}{3} \frac{d[Q]}{dt} = \frac{1}{4} \frac{d[R]}{dt} = \frac{1}{5} \frac{d[S]}{dt}$$

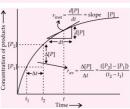
Average rate of reaction: It is the rate measured over a long time interval.

Average rate of reaction =
$$\frac{\Delta x}{\Delta t}$$

Instantaneous rate of reaction: It is the rate at any moment, i.e., when time interval is very small.

Instantaneous rate of reaction = $\frac{dx}{dt}$





Factors Affecting Rate of Reaction

- Concentration of the reactants: In most cases, rate of a reaction increases by increasing the concentration of reactants.
- Presence of a catalyst : A catalyst increases the rate of a reaction.
- ☐ Temperature of the reaction : Usually reactions are faster at higher temperatures.
- □ Nature of reactants : Rate of reaction depends on nature of reactants i.e., the type of bonds which have to be broken for reaction to occur.
- □ Exposure to light : Normally reactions proceed faster in presence of light.
- Surface area of solid reactant: Reactions involving a solid with liquid or gas occur on surface and are faster when surface area is more.

Law of Mass Action

- This law was given by Guldberg and Waage,
- According to this law,
 - "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to the powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction".
- Active mass = Molar concentration of the substance

$$= \frac{n}{V} = \frac{w}{MV}$$

For the reaction.

$$aA + bB \longrightarrow mM + nN$$

Rate,
$$r \propto [A]^a [B]^b$$

$$r = k[A]^a [B]^b$$

where k is the proportionality constant named as rate constant.

Rate Constant

For the reaction.

$$A \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]$$

If
$$[A] = 1$$
 then $\frac{dx}{dt} = k$

For the reaction.

$$aA + bB \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^a [B]^b$$

$$f[A] = [B] = 1, \text{ then } \frac{dx}{dt} = \frac{dx}{dt} = \frac{dx}{dt}$$

If
$$[A] = [B] = 1$$
, then $\frac{dx}{dt} = k$

- O Thus, at a given temperature, the rate constant or specific reaction rate or velocity constant of a reaction, is equal to the rate of the reaction when the concentration of each of the reactants is unity.
- Units of rate constant: Units of rate constant are different for different order of reactions.

For the general reaction,

$$aA + bB \longrightarrow cC + dD$$

Rate =
$$k[A]^x [B]^y$$

where, x and y are the active moles of reactants A and B respectively.

Hence, x + y = n = order of reaction

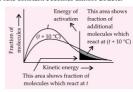
$$k = \frac{\text{Rate}}{[A]^x [B]^y}$$

$$= \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$$

SI unit of concentration is mol L-1 and that of time is s.

Factors Affecting Rate Constant

- Concentration: The value of rate constant for a reaction does not depend upon the concentration of the reactants.
- Temperature: For every 10°C rise in temperature. the rate constant becomes almost double.



Molecularity of Reaction

- It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction. which must collide simultaneously in order to bring about a chemical reaction.
- Depending on the number of reacting molecules, reaction can be unimolecular, bimolecular or trimolecular.
 - The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

 Bimolecular reactions involve simultaneous collision between two species, for example, dissociation of hydrogen iodide.

$$2HI \longrightarrow H_2 + I_2$$

- O Trimolecular or termolecular reactions involve simultaneous collision between three reacting species, for example, $2NO + O_2 \longrightarrow 2NO_2$
- Molecularity above three is not usually seen.
- The overall molecularity of a complex reaction is equal to the molecularity of the slowest (rate determining) step.
 - For example,

Decomposition of
$$H_2O_2$$
:
 $2H_2O_2 \longrightarrow 2H_2O + O_2$

Mechanism:

$$H_2O_2 \xrightarrow{\text{slow}} H_2O + O$$

 $H_2O_2 + O \xrightarrow{\text{fast}} H_2O + O_2$

Rate = $k[H_2O_2]$, Molecularity = 1

Order of Reaction

It is defined as, the number of molecules of reactants whose concentration determines the rate law expression or it is the sum of the exponents to which the concentration terms must be raised to express the rate of reaction from experimental data.

- For the reaction,
 - $aA + bB \longrightarrow Products$
 - According to rate law,
 - Rate = $k[A]^x [B]^y$
 - Order of reaction = x + y
 - For examples,

$$^{ \bullet } \quad N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + \frac{1}{2}\,O_{2(g)};$$

- $r = k[N_2O_5]$ Order = 1
- \bigcirc 2NO_{2(g)} \longrightarrow 2NO_(g) + O_{2(g)}; $r = k[NO_3]^2$ Order = 2
- O 2NO_(g) + O_{2(g)} \longrightarrow 2NO_{2(g)} $r = k[NO]^2[O_2]$ Order = 3
- O CH₂CHO → CH₄ + CO;
- $r = k[CH_3CHO]^{3/2}$ Order = 3/2 $2NH_2 \longrightarrow N_2 + 3H_2$: $r = k[NH_2]^0$

Order = 0

Comparison between Molecularity and Order of Reaction

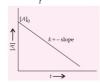
Molecularity of reaction	Order of reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of the reacting species in rate law.
It is a theoretical concept.	It is an experimental quantity.
It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer (may range from 0 to 3).
It is independent of pressure and temperature.	It depends upon pressure and temperature.

Types of Order of Reactions

 Zero order reaction: In a zero order reaction, rate is independent of the concentration of reactant. For the reaction,

For the reaction,

$$t = 0$$
 $A \longrightarrow Products$
 $t = 0$ $A \longrightarrow Products$
At time t $(a - x)$ x
Rate $= \frac{dx}{dt} = k[A]^0 = k(a - x)^0$
On integration, $k = \frac{x}{t}$ or $x = kt$



- Examples of zero order reaction
 - The photochemical combination of H₂ and
 - Decomposition of ammonia on a hot platinum surface at high pressure.
- First order reaction : In the first order reaction. rate is determined by the change of one concentration term only.

For the reaction,

$$A \longrightarrow Products$$

Rate =
$$\frac{dx}{dt}$$
 = $k(a-x)$ or $\frac{dx}{(a-x)}$ = $k dt$

On integration,
$$\int \frac{dx}{(a-x)} = k \int dt$$

$$i.e. - \ln(a - x) = kt + c$$

where c is an integration constant,
when
$$t = 0$$
, $x = 0$ then

$$-\ln a = c$$

 $\ln -\ln(a-x) = kt - \ln a$

or
$$kt = \ln a - \ln (a - x)$$
 or $kt = \ln \frac{a}{(a - x)}$

$$k = \frac{1}{t} \ln \frac{a}{(a-x)} = \frac{2.303}{t} \log \frac{a}{(a-x)}$$



- O $T = n \times t_{1/2}$ where T = total time and n = number of half-lives. For a first order reaction $T_{75} = 2 \times T_{50}$; $T_{875} = 3 \times T_{50}$; $T_{999} = 10 \times T_{50}$
- Examples of first order reaction
 - $C_{12}H_{22}O_{11} + H_2O \xrightarrow{acid} C_6H_{12}O_6 + C_6H_{12}O_6$
 - \circ SO₂Cl₂ \longrightarrow SO₂ + Cl₂
 - All radioactive decays
 - O NH₄NO₂ \longrightarrow N₂ + 2H₂O
- Second order reaction: In the second order reactions, rate is determined by the variation of two concentration terms or second power of concentration.
 - When both the reactants are the same.

For the reaction,

2A → Products

$$\frac{dx}{dt} = k(a-x)^2$$

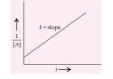
On integration,
$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

 When two different reactants having initial concentration a and b react with each other as given below

$$A + B \longrightarrow Products$$

$$\frac{dx}{dt} = k(a-x)(b-x)$$

On integration,
$$k = \frac{1}{t} \cdot \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$$



- Examples of second order reaction
 - The hydrolysis of ester in presence of alkali
 - O 2O₃ \longrightarrow 3O₂
 - O $2N_2O \longrightarrow 2N_2 + O_2$
- Third order reaction: A reaction is said to be of the third order if the rate of reaction depends upon three concentration terms.

 $A + B + C \longrightarrow Products$

 $2A + B \longrightarrow Products$

3A → Products

The simplest case in the reaction of last type. The expression for the rate constant of such a reaction may be:

For the reaction,

$$3A \longrightarrow Products$$

$$\frac{dx}{dt} = k(a-x)^3$$

On integration, $k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$

$$= \frac{1}{2t} \frac{x}{a^2} \frac{(2a-x)}{(a-x)^2}$$



- Examples of third order reaction
 - 2FeCl₃ + SnCl₂ → SnCl₄ + 2FeCl₂
 - $2NO + Br_2 \longrightarrow 2NOBr$
- nth order reaction: In general, a reaction of the nth order, where all the initial concentrations are the same, has a reaction rate

$$\begin{split} \frac{dx}{dt} &= k_n (a - x)^n \\ k_n &= \frac{1}{(n - 1)t} \left[\frac{1}{(a - x)^{n - 1}} - \frac{1}{(a)^{n - 1}} \right] \\ t_{1/2} &\simeq \frac{1}{a^{(n - 1)}} \text{ or } t_{1/2} &\simeq a^{(1 - n)} \text{ or } t_{1/2} = \frac{2^{n - 1} - 1}{k_n (n - 1)(a)^{n - 1}} \end{split}$$

Half-life of Reaction $(t_{1/2})$

 It is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where, n is the order of the reaction.

- Fractional order reaction: There are some reactions for which order of reaction is not an integer.
 - e.g. Decomposition of CH₃CHO CH₃CHO \longrightarrow CH₄ + CO Rate = kICH₂CHOl^{3/2}
- Negative order reaction: There are some reactions for which rate of reaction decreases as the concentration of one of the constituent increases. A negative reaction order just means that if we increase the concentration of the reactant, the reaction rate will decrease.

e.g. $2O_3 \longrightarrow 3O_2$

Rate = $k[O_3]^2[O_2]^{-1}$

Therefore, the order of reaction with respect to oxygen is -1.

Pseudounimolecular Reaction

CH2COOCH3 + H2O acid CH2COOH + CH2OH

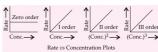
According to law of mass action, given reaction should be bimolecular, but as water is present in large excess, its concentration remains practically constant, so, does not affect the rate of reaction. Hence reactions showing such a behaviour are called pseudounimolecular reactions and also known as pseudo first order reactions.

Summary of rate law, integrated rate law, half-life, unit of rate constant and graph for the reactions of different orders:

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L ⁻¹ s ⁻¹	[A] $vs\ t$; slope = $-k$
1	Rate = $k[A]^1$	$ln[A]_t = -kt + ln [A]_0$	$t_{1/2} = 0.693/k$	s ⁻¹	ln[A] vs t; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k [A]_0$	L mol ⁻¹ s ⁻¹	1/[A] vs t; slope = k
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	$t_{1/2} = 1/k \ [A]_0$	L mol ⁻¹ s ⁻¹	1/[A] vs t ; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol } L^{-1})^{1-n} s^{-1}$	$\frac{1}{[A]^{n-1}} vs t;$ $slope = k$

Methods of Determining Order of Reaction

- Method of integration (Hit and Trial method): It involves the substitution of experimental values of a and x at a given time, in different rate equations.
 - The equation which gives constant value of k will suggest the order.
 - If all the reactants are at the same molar concentrations, the kinetic equations are:
 - For zero order reaction, $k = \frac{1}{4}(a_0 a)$
 - For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$
 - For second order reaction, $k = \frac{1}{t} \left[\frac{1}{(a-x)} \frac{1}{a} \right]$
 - For third order reaction, $k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} \frac{1}{a^2} \right]$
- Graphical method: It involves determining the rate for a given change at different concentrations of reactants.
 - Graphs are then plotted between rates and concentrations, the nature of which suggest the order.



I Fractional change method (Half-life method): It involves conducting the reaction at different concentrations and determining time required to

It involves the use of the general expression for the half-life and plotting the half-life $(t_{1/2})$ vsconcentration (a^{1-n}) .

i.e.,
$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

For zero order reaction, t_{1/2} ∝ a

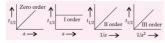
complete a definite fraction.

- For first order reaction, t_{1/2} is independent of a, i.e. t_{1/2} = constant.
- For second order reaction, t_{1/2}

 1/a,
 i.e. t_{1/2} a = constant.
- For third order reaction, $t_{1/2} \propto \frac{1}{a^2}$,

i.e. $t_{1/2} a^2 = \text{constant}$

- In general, for n^{th} order reaction, $t_{1/2} \propto \frac{1}{a^{n-1}}$, i.e. $t_{1/2} a^{n-1} = \text{constant}$.
 - Thus, the nature of dependence of $t_{1/2}$ on the concentration of the reactant will give the order of the reaction.



Effect of Temperature

The rates of many reactions are approximately doubled or tripled for every $10^{\circ}\mathrm{C}$ rise in temperature.

Temperature coefficient (
$$\mu$$
) = $\frac{k_{t+10}}{k_t}$ = 2 or 3

■ Arrhenius equation : $k = Ae^{-E_a/RT}$

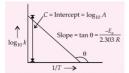
$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303 \, RT}$$

where k = rate constant,

A = pre-exponential factor (frequency factor) $E_a = \text{activation energy,}$

T = temperature

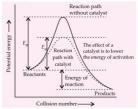
$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \, R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$



Effect of Catalyst

- A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- ☐ It participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex which decomposes to yield products and the catalyst.
- It provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.
- Positive catalyst: Substances that increase the reaction rate by changing the path of reaction and lowering the activation energy.
- Catalystinhibitors/Negative catalyst: Substances that reduce the action of catalysts reversibly.

- Catalyst poisons: Substances that reduce the action of catalysts irreversibly.
- Catalyst promotors: Substances that increase the catalytic activity, even though they are not catalysts by themselves.



Collision Theory of Chemical Reaction

- According to this theory
 - Molecules must collide to react.
 - When colliding molecules possess a certain minimum energy only then products are formed, such collisions are called effective collisions.
 - For effective collision, molecules must have a minimum (threshold) energy, molecules having lesser energy have to be given this additional energy, called activation energy.
 - Activation energy = Threshold energy -

Energy of colliding molecules

 Apart from possessing threshold energy, the molecules should be properly oriented to result in the formation of new bonds.
 k = PZ_e-f_e/RT

where *Z* is collision frequency and *P* is steric factor.

Activated Complex Theory

According to this theory

- Breaking of old bonds in reactant molecules and formation of new bonds occur simultaneously.
- At some stage an activated complex or transition state, is formed with old bonds partially broken and new ones partially formed.
- Energy of the activated complex is higher than that of reactants and products.
- The reactants do not directly yield the products. They have to cross the activated complex state, called energy barrier.
- Height of energy barrier determines the threshold energy.

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UNIT-8

Biomolecules | Polymers | Chemistry in Everyday Life

BIOMOLECULES

- Introduction
- · Classification, structure, importance
- Carbohydrates
- Proteins
- Vitamins
- Nucleic acids

TIPS TO REMEMBER

Carbohydrates (Sugars or Saccharides)

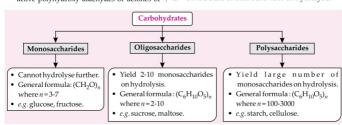
□ Carbohydrates are primarily produced by plants and form a very large group of naturally occurring organic compounds. e.g., cane sugar, glucose, starch, etc. Most of them have a general formula, C₄(H₂O)_y, and were considered as hydrates of carbon.

$$xCO_2 + yH_2O \xrightarrow{\text{Sunlight}} C_x(H_2O)_y + xO_2$$

 Chemically, they may be defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.

Classification

- Reducing sugars: Contain free aldehydic or ketonic group and reduce Fehling's solution and Tollens' reagent.
 - All monosaccharides and disaccharides having free aldehydic or ketonic group are reducing sugars. e.g., maltose and lactose.
- Non-reducing sugars: Do not have free aldehydic or ketonic group and do not reduce Fehling's solution and Tollens' reagent.
 - In disaccharides, if the reducing groups of monosaccharides, i.e. aldehydic or ketonic groups are bonded, they are non-reducing in nature. e.g., sucrose.
 - On the basis of their behaviour on hydrolysis:



Nomenclature

The names of the simpler carbohydrates end in -ose. Carbohydrates with an aldehydic structure are known as aldoses and those with ketonic structure as ketoses. The number of carbon atoms in the molecule is indicated by a Greek prefix.

Number of C atoms in the molecule	Aldose	Ketose
3	Aldotriose	Ketotriose
4	Aldotetrose	Ketotetrose
5	Aldopentose	Ketopentose
6	Aldohexose	Ketohexose
7	Aldoheptose	Ketoheptose

MONOSACCHARIDES

Glucose

- □ Glucose is an aldoses monosaccharide with formula C₆H₁₂O₆. As it has six carbon atoms so categorized as aldohexose also known as dextrose
- It occurs in ripe grapes, honey and most of the sweet fruits and also known as grape sugar.
- It is the monomer of many of the large carbohydrates, namely starch, cellulose etc.
- Preparation
 - Laboratory method : From sucrose (cane sugar)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

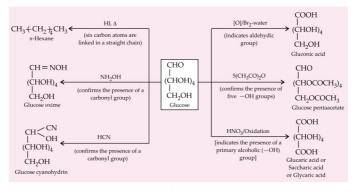
Sucrose Fructose

Commercial method: From starch

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+/\Delta} nC_6H_{12}O_6$$

Starch or Cellulose

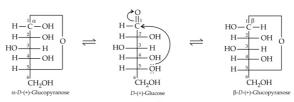
Structure



The exact spatial arrangement of different
 OH groups was given by Fischer.



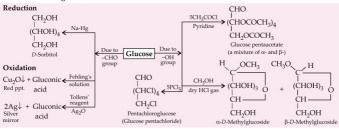
- Despite having the aldehyde group, it does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with NaHSO₃.
- The pentaacetate of it does not react with hydroxylamine indicating the absence of free
 CHO group in glucose pentaacetate.
- The above behaviour could not be explained by the open chain structure.



 The cyclic structure of glucose is represented by Haworth structure.

- α and β-D-glucose have different configuration at anomeric (C-1) carbon atom, hence are called anomers and the C-1 carbon atom is called anomeric carbon (glycosidic carbon).
- The six membered cyclic structure of glucose is called pyranose structure.

Other reactions of glucose



Tests

Reagents	Observations
With little conc. H ₂ SO ₄	Charred residue of carbon.
With dilute NaOH	First yellow and then brown.
Molisch's test : Two drops of alcoholic solution of $\alpha\text{-naphthol}+2$ drops of carbohydrate + conc. H_2SO_4 along the sides of test tube.	Violet ring at the junction of two liquids.
Silver mirror test: With Tollens' reagent	Silver mirror appears.
With Fehling's solution	Red ppt. of Cu ₂ O.

Fructose

- Fructose is a keto hexoses as it contains six carbon and ketonic group. It has general formula C₆H₁₂O₆.
- It is present in abundance in fruits and hence is called fruit sugar.
- Naturally occuring fructose is laevorotatory so also known as laevulose.
 - In the combined state, it is present in disaccharide as sucrose and polysaccharide as inulin.

Preparation

From sucrose (cane sugar)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{dil. } H_2 > O_4} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
Cane sugar
(Dextrorotatory)
(Dextrorotatory)
(Dextrorotatory)
(Laevorotatory)

The solution contains equimolar mixture of *D*-(+)-glucose and *D*-(-)-fructose is called *invert* sugar and the process is known as *inversion*.

From inulin

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{dil. } H_2SO_4} nC_6H_{12}O_6$$
Inulin Fructose

Structure

On the basis of its reactions, it was found to contain a ketonic functional group at C-2 atom and six carbon atoms in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(-)-fructose. Its open chain structure is as shown:

$$CH_2OH$$
 $C=O$
 $C=O$
 $C=O$
 $C=O$
 $C=O$
 $C=O$
 $C=O$
 CH_2OH
 CH_2OH
 CH_2OH
 CH_2OH

 It also exists in two cyclic forms which are obtained by the addition of — OH at C-5 to the (>C = O) group. The ring, thus formed is a five membered ring and is named as furance.

 The cyclic structures of two anomers of fructose are represented by Haworth structures.

Mutarotation

- Glucose and fructose exists in two isomeric forms, i.e., α -D-glucose (specific rotation = + 112°) and β -D-glucose (specific rotation = + 19°). However, when aqueous solution of either of these two forms allowed to stand, it gets converted into the some equilibrium mixture of both the α and the β -forms with a small amount of the open chain form.
 - As a result of this equilibrium, the specific rotation of a freshly prepared solution of α-D-glucose decreases from +112° to +52.7° while that of β-D-glucose increases from +19° to 52.7°.

 $\alpha\text{-}D\text{-}Glucose \Longrightarrow \text{Equilibrium} \Longrightarrow \beta\text{-}D\text{-}Glucose$ mixture

$$\left[\alpha\right]_D = +\ 112^\circ \qquad \left[\alpha\right]_D = +\ 52.7^\circ \qquad \left[\alpha\right]_D = +\ 19^\circ$$

- This change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation. All monosaccharides and reducing disaccharides undergo mutarotation. Fructose also undergoes mutarotation.
 - α -D-Fructose \rightleftharpoons Equilibrium \rightleftharpoons β -D-Fructose mixture $[\alpha]_D = -21^\circ \qquad [\alpha]_D = -92^\circ \qquad [\alpha]_D = -133^\circ$

■ Comparison of Glucose and Fructose

Property	Glucose	Fructose	
Molecular formula	C ₆ H ₁₂ O ₆	C ₆ H ₁₂ O ₆	
Nature	Polyhydroxy aldehyde	Polyhydroxy ketone	
Optical activity of natural form	Dextrorotatory	Laevorotatory	
Oxidation			
(a) with bromine water	Gluconic acid	No reaction	
(b) with conc. nitric acid	Saccharic acid (glucaric acid)	Mixture of glycollic acid, tartaric acid and trihydroxy glutaric acid	

Reduction with NaBH $_4$ or Na-Hg/ H_2O	D-Sorbitol	Mixture of <i>D</i> -sorbitol and <i>D</i> -mannitol	
Fehling's solution	Gives red precipitate	Gives red precipitate	
Tollens' reagent	Forms silver mirror	Forms silver mirror	
Resorcinol + HCl (dil.) (Selivanoff's test)	No colouration	Gives red or brown colour or precipitate	
Freshly prepared ammonium molybdate sol. + few drops of acetic acid (Pinoff's test)	Light blue colour	Bluish green colour on heating	
Alcoholic α-naphthol + HCl (conc.) (Furfural test)	No colouration	A purple colour (violet) on boiling	

DISACCHARIDES

 Disaccharides are formed when two monosaccharides are joined together by an oxide linkage (glycosidic linkage) formed by the loss of a water molecule.

Sucrose (Cane sugar)

Preparation

$$\begin{array}{c} C_{12}H_{22}O_{11(s)} + H_{2O} & \xrightarrow{\text{Hydrolysis}} \\ (+)\text{Sucrose} \\ [\alpha]_D *+ 66.5^\circ & \underbrace{C_6H_{12}O_{6(\alpha_0)} + C_6H_{12}O_{6(\alpha_0)}}_{\text{Invert sugar}} \\ D-(+)\text{-Fluctose } [\alpha]_D + 52.7^\circ \text{ and } \\ D-(-)\text{-Fructose } [\alpha]_D = -92.4^\circ \end{array}$$

- Structure: It is a disaccharide in which two monosaccharides are held together by a glycosidic linkage between C-1 of α-glucose and C-2 of β-fructose.
 - Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.

It is dextrorotatory in nature.

Maltose

Preparation

$$2(\mathsf{C}_6\mathsf{H}_{10}\mathsf{O}_5)_n + n\mathsf{H}_2\mathsf{O} \xrightarrow{\quad \mathsf{Hydrolysis} \quad} n\mathsf{C}_{12}\mathsf{H}_{22}\mathsf{O}_{11}$$

$$\xrightarrow{\quad \mathsf{Maltose} \quad} \mathsf{Maltose}$$

Structure: It is a disaccharide in which two α-D-glucose units are held together by a glycosidic linkage between C-1 of one glucose unit and C-4 of another elucose unit.

 It is a reducing sugar and dextrorotatory in nature.

Lactose (Milk sugar)

Preparation

$$\begin{array}{c} C_{12}H_{22}O_{11(s)}+H_2O \xrightarrow{\quad Hydrolysis \\ \quad Lactase \quad \quad \\ \quad C_6H_12O_6 \quad + \quad C_6H_{12}O_{6(ag)} \\ \quad D_{(+)}\text{-Glucose} \quad D_{(+)}\text{-Glactose} \end{array}$$

Structure: It is a disaccharide of β-D-galactose and β-D-glucose which are held together by a glycosidic linkage between C-1 of galactose and C-4 of glucose.

 It is a reducing sugar and epimeric in nature.

POLYSACCHARIDES

- Carbohydrates which yield a large number of monosaccharides on hydrolysis are called polysaccharides. e.g. starch, cellulose, glycogen, gums, etc.
- They mainly act as the food storage or structural materials.
- They are non-reducing in nature due to absence of free aldehydic or ketonic group.

Starch

- Starch is the main storage polysaccharide of plants. It is a polymer of α-D-glucose units and consists of two components—amylose and amylopectin.
 - Amylose is water soluble component which constitutes about 15-20% of starch. Chemically, amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held by 1,4-α-glycosidic linkage.

 Amylopectin is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α-D-glucose units in which chain is formed by 1,4-α-glycosidic linkage whereas branching occurs by 1,6-α-glycosidic linkage.

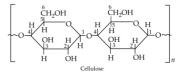
Structure

Cellulose

- Cellulose is present in plants. It is not digestible by human beings.
- It is the major constituent of cell wall of plant cells.

It is a straight chain polysaccharide composed only of β-D-glucose units which are joined together by 1,4-β-glycosidic linkages i.e., the β-glycosidic linkages between C-1 of one glucose and C-4 of the next glucose unit.

Structure



Glycogen

- Glycogen is the carbohydrate which is stored in animal body. It is also known as animal starch.
 When the body needs glucose, enzymes break the glycogen down to glucose.
- It is a major constituent of liver, muscles and brain.
- It is also found in yeast and fungi.

Key Points

- Humans do not contain enzyme, cellulase which hydrolysis cellulose into glucose.
- Cellulase is present in the stomach (rumen) of ruminant animals such as cow, buffalo, etc. and hence cellulose is easily digestible by them.

Importance

- They are storage molecules as starch in plants and glycogen in animals. Cell wall of bacteria and plants is made up of cellulose.
- They are used in the form of wood, as furniture and clothe ourselves with cellulose in the form of cotton fibres.
- They provide raw materials for many important industries like textiles, paper, lacquers and breweries.
- They are the major components of nucleic acids, RNA and DNA.

PROTEINS

Proteins are the biomolecules of the living system made up of nitrogenous organic compounds by condensation polymerisation of α-amino acids.

Major sources of proteins are milk, cheese, pulses, fish, meat, peanuts, etc.

Amino acids

- Amino acids are the bifunctional molecules with both acidic carboxylic group (- COOH) and basic amino group (- NH2).
- \Box In α-amino acids, the amino (- NH₂) group is at α-position w.r.t. carboxylic (- COOH) group. i.e., both amino and carboxylic groups are attached to the same carbon atom.
- ☐ They are very important as they are the building blocks of proteins.

$$\begin{array}{c|c}
NH_2 \\
R - C - COOH \\
R = side chain) \\
H \\
\alpha-Amino acid
\end{array}$$

Name of amino acid	Structure of R	Three letter symbol
Glycine	-H	Gly
Alanine	-CH ₃	Ala
*Valine	-CH(CH ₃) ₂	Val
*Leucine	-CH ₂ CH(CH ₃) ₂	Leu
*Isoleucine	-CH-CH ₂ -CH ₃ CH ₃	Ile
*Arginine	– (CH ₂) ₃ NH– C – NH ₂ II NH	Arg
*Lysine	-(CH ₂) ₄ NH ₂	Lys
Glutamic acid	-CH ₂ CH ₂ COOH	Glu
Aspartic acid	−CH ₂ COOH	Asp
Glutamine	-CH ₂ CH ₂ CONH ₂	Gln
Asparagine	-CH ₂ CONH ₂	Asn
*Threonine	-CH(OH)CH ₃	Thr
Serine	-CH ₂ OH	Ser
Cysteine	-CH ₂ SH	Cys
*Methionine	-CH ₂ CH ₂ SCH ₃	Met
*Phenylalanine	-CH ₂ C ₆ H ₅	Phe
Tyrosine	-CH ₂ C ₆ H ₄ OH(p)	Tyr
*Tryptophan	HN——	Trp

*Histidine	−CH ₂ NH N=	His
Proline	HN COOH	Pro
*Essential amino a	cids	

Classification of Amino acids

 Depending upon the relative number of amino (— NH₂) and carboxyl (— COOH) groups.

Neutral

No. of -COOH groups = No. of $-NH_2$ groups e.g., Glycine, Alanine, Valine

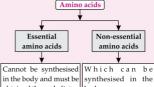
Acidic

No. of -COOH groups > No. of -NH2 groups e.g., Aspartic acid, Asparagine, Glutamic acid

Basic

No. of -NH2 groups > No. of -COOH groups e.g., Lysine, Arginine, Histidine

On the basis of their synthesis:



obtained through diet. body. E.g. valine, leucine, E.g. glycine, alanine, lysine, isoleucine, glutamic acid, arginine, etc. aspartic acid, etc.

Physical Properties

- Amino acids are usually colourless, crystalline, water soluble and high melting solids.
- They behave like salts due to presence of basic amino group (- NH2) and acidic carboxylic group (- COOH) in the same molecule.

 In aqueous solution, the carboxylic group can lose a proton and amino group can accept a proton giving rise to a dipolar ion known as zwitter ion. This is neutral but contains both positive and negative charges.

$$\begin{array}{ccc} & & & & & & & & & & & \\ R-CH-C-OH & \Longrightarrow & R-CH-C-O' \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$$

Chemical Properties

- O Since these form salts with acids as well as with bases, their chemical reactions are similar to primary amines and carboxylic acids. Compounds which exhibit acidic and basic properties are called amphoteric substances and the phenomenon is known as amphoterism.
- The equilibria are expressed as follows:

• Isoelectric point: The pH at which dipolar ion (zwitter ion) exists as neutral ion, i.e., +ve and -ve charge is equal and it does not migrate to either electrode, is called isoelectric point. The amino acids have least solubility in water at isoelectric point which helps in their separation.

Key Points

- Except glycine, all other naturally occurring α-amino acids are optically active because they contain chiral, asymmetric carbon atom
- They exist in both *D* and *L*-forms. Most naturally occurring α-amino acids have *L*-configuration.
- L-Amino acids are represented by writing the – NH₂ group on the left hand side.

COOH
$$H_2N \stackrel{\alpha}{-} \stackrel{\Gamma}{C} - H$$

$$R$$

$$L-Amino acid$$

Peptides and their classification

Peptide bond: The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond.

- The products formed by the linking of amino acids by peptide linkage are known as peptides.
- Peptides are further divided into di, tri, tetra depending upon the number of amino acids combined.
- Oligopeptide contains anywhere between 2-10 amino acids. Structures with more than ten amino acids are known as polypeptides.

$$\begin{array}{c|c} H_2N-CH-C & NH-CH-C \\ R & N' \\ N \\ N \\ N \\ \text{terminal} \\ \text{amino acid} \end{array} \begin{array}{c} O \\ NH-CH-C \\ N' \\ N \\ N \\ \text{Terminal} \\ \text{amino acid} \end{array}$$

R, R', R'' may be same or different.

 A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u is called a protein.

Classification of Proteins

 On the basis of molecular structure, proteins are classified as fibrous and globular proteins.

Fibrous proteins

In fibrous proteins, polypeptide chains are parallel and are held together by hydrogen and disulphide bonds. These are insoluble in water, e.g., keratin and myosin.

Globular proteins

Globular proteins results when the polypeptide chains coil around to give three dimensional spherical shape. These are soluble in water, e.g., insulin and albumins.

Structure

Proteins have complex structure. Structure and shape of proteins can be studied at four different levels, viz, primary, secondary, tertiary and quaternary. Each level is more complex than the previous one.

Primary structure

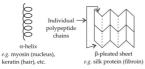
It refers to number and linear sequence of amino acids held together by peptide bonds.

Primary structure

- It determines different chemical and biological properties of proteins.
- O Any change in the sequence may affect the function and properties of protein.

Secondary structure

- The peptide chain assumes a secondary structure by folding or coiling.
- O The linkage or bonds involved in the secondary structure formation are hydrogen bonds and disulphide bonds.
- It is mainly of two types:
 - α-helix: These coils are stabilized by hydrogen bonds between carbonyl oxygen of first amino acid to amide nitrogen of fourth amino acid.
 - β-pleated sheet structure: β-pleated sheet structure is formed when hydrogen bonds are formed between the carbonyl oxygens and amide hydrogens of two or more adjacent polypeptide chains. The bonding in β-pleated sheet structure is intermolecular H-bonding. The structure is not planar but is slightly pleated. Silk fibroin is rich in β-pleated sheets.



Tertiary structure

- It represents overall folding of the polypeptide chains, i.e., further folding of the secondary structure.
- The bonds responsible for such interaction are as follows:
 - Hydrophobic interactions
 - Hydrogen bonds
 - Ionic or electro-interactions
 - van der Waals' forces
 - Disulphide bonds

- O These are of two types:
 - Tertiary structure of fibrous protein has same secondary (α-helix or β-pleated) structure throughout the length of the
 - Tertiary structure of globular protein does not have the same secondary structure throughout the length of the molecule. Parts of the molecule may have α-helical structure, while the other part may have β-pleated sheet structure.

Ouaternary structure

Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

Denaturation of proteins

- O When a protein in its native form, is subjected to physical changes like change in temperature or chemical changes like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.
- The denaturation causes change in secondary and tertiary structures but primary structure remains intact.
- Some examples of denaturation of proteins
 - coagulation of egg white on boiling.
 - curdling of milk.
 - formation of cheese, when an acid is added to milk.

Key Points

- Denaturation of proteins may be reversible or irreversible.
- The reverse process is called renaturation.
- When the changes under which the native protein is stable, are brought back, secondary and tertiary structures of the proteins are restored.
 - Renaturation results in recovery of the biological activity.

Importance

- They serve as
 - major structural material of animal tissues.
 - transport agent.
 - as enzymes to carry out many biological reactions.
 - metabolic regulator.
 - antibodies to defend the body against foreign substances called antigens.

ENZYMES

The enzymes are biocatalysts produced by living cells which catalyse biochemical reactions in living organisms. Chemically, enzymes are naturally occurring simple or conjugated proteins. Some enzymes may be non-proteins also.

Enzyme	Reaction catalysed
Maltase	Maltose → Glucose + Glucose
Lactase	Lactose → Glucose + Galactose
Amylase	$Starch \rightarrow n \times Glucose$
Invertase	$Sucrose \rightarrow Glucose + Fructose$
Pepsin	Proteins $\rightarrow \alpha$ -Amino acids
Trypsin	Proteins $\rightarrow \alpha$ -Amino acids
Urease	$Urea \rightarrow CO_2 + NH_3$
Nuclease	DNA, RNA \rightarrow Nucleotides
Emulsin	Cellulose $\rightarrow n \times Glucose$

Properties

- Enzymes are needed in very small amount.
- They reduce magnitude of activation energy.They are highly specific.
- They work at specific pH.
- They work well at moderate temperature.

Mechanism

 Binding of the enzyme (E) to substrate (S) to form a complex called the enzyme-substrate complex.

$$E + S \longrightarrow ES$$

 Formation of complex of enzyme and product.

$$ES \longrightarrow EP$$

 Release of product from the enzyme-product complex.

$$EP \longrightarrow E + P$$

Importance

- They play a vital role in living organisms as they catalyse many biological processes.
- Even its deficiency causes diseases e.g., the deficiency of phenylalanine hydroxylase enzyme causes phenyl ketone urea (PKU) and the deficiency of tyrosinase causes albinism.
- They are used for the production of beer, wine, syrup and cheese also.

VITAMINS

These are complex organic molecules which cannot be produced by the body and must be supplied in small amounts in diet to carry out essential metabolic reactions which are required for normal growth and maintenance of the body.

Classification

Vitamins

Water soluble vitamins Soluble in water.

- Must be supplied regularly in diet as they are regularly excreted in urine (except vitamin B₁₂).
- E.g., Vitamin B_1 , B_2 , B_6 , B_{12} and C

Fat soluble vitamins

- Soluble in fat and oils.
- · Stored in liver and adipose tissues.
 - E.g., Vitamin A, D, E and K

Vitamin name	Chemical name	Solubility	Sources	Deficiency disease
Vitamin A	Retinoids (retinol, retinoids and carotenoids)	Fat	Milk, butter, eggs, fish, cod liver oil, green vegetables, etc.	Night-blindness, xerophthalmia
Vitamin B ₁	Thiamine	Water	Pulses, nuts, cereals (rice, wheat, etc.), rice bran, yeast, egg yolk, fruits and green vegetables, etc.	Beri-beri, loss of appetite
Vitamin B ₂	Riboflavin	Water	Milk, green vegetables, egg white, meat, liver, kidney, etc.	Anaemia, inflammation of tongue, dermatitis, cheilosis
Vitamin B ₆	Pyridoxine	Water	Rice bran, whole cereal (wheat, gram), yeast, fish, meat, eggs, etc.	Affects central nervous system, causes weakness, convulsions, insomnia, anaemia

Vitamin H	Biotin	None	Milk, yeast, liver, kidney, etc.	Dermatitis
Vitamin B ₁₂	Cyanocobalamin	Water	Eggs, milk, liver of ox, sheep, fish, etc.	Pernicious anaemia
Vitamin C	Ascorbic acid	Water	Citrus fruits, chillies, sprouted pulses, etc.	Pyorrhea, scurvy (bleeding of gums)
Vitamin D (a mixture of vitamins D ₁ and D ₃)	Ergocalciferol and cholecalciferol	Fat	Butter, milk, eggs, fish liver oil, liver and meat (Vitamin D_3 is produced in skin in presence of sunlight).	
Vitamin E	Tocopherol	Fat	Wheat germ oil, milk, nuts, peanut oil, cotton seed oil, eggs, fish, etc.	
Vitamin K	Phylloquinone	Fat	Leafy vegetables like cabbage, spinach, etc.	Haemorrhages and lengthens time of blood clotting

Key Points

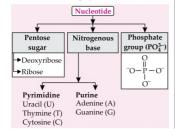
- Deficiency of more than one vitamin in the body causes many diseases. This condition is known as avitaminosis.
- Excess intake of vitamins (A and D) may cause hypervitaminoses.
- Vitamin H (biotin) is neither soluble in water nor in fats.
- Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them. However, the bacteria of the gut can produce some of the vitamins required by us.

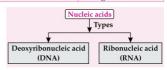
NUCLEIC ACIDS

They are the polynucleotides present in nucleus of all living cells. They play an important role in transmission of the hereditary characteristics and biosynthesis of proteins.

Chemical Composition of Nucleic Acids

Nucleic acids are the polymers of nucleotides.





Pentose sugar

 Deoxyribose: It is also a carbohydrate (sugar) containing five carbon atoms but one oxygen less than ribose. It is present in DNA.

 Ribose: It is a carbohydrate (sugar) containing five carbon atoms. It is present in RNA.

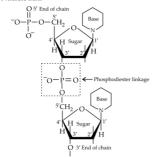
 Nitrogenous base: These are heterocyclic organic compounds having two or more nitrogen atoms in the ring.

Structure

 A unit formed by attachment of a base to 1' position of sugar is known as nucleoside.

- The carbon atoms of the sugars are numbered as 1', 2', 3', etc in order to distinguish from bases
- When nucleoside is linked to phosphoric acid at 5' position of sugar moiety, we get a nucleotide.
- Nucleotides are joined together by phosphodiester linkages between 5' and 3' carbon atoms of pentose sugar.

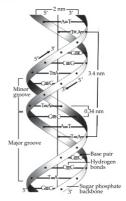
Nucleic acid



 Two types of nucleic acids, viz, DNA and RNA are distinguished from each other in the following manner:

Deoxyribonucleic acid (DNA)	Components	Ribose nucleic acid (RNA)
2-deoxy-D-(-) ribose	Sugar	D-(-)ribose
Cytosine and thymine	Pyrimidine base	Uracil and cytosine
Adenine and guanine	Purine base	Adenine and guanine
H ₃ PO ₄	Phosphoric acid	H ₃ PO ₄
Double stranded α-helix	Structure	Single stranded α-helix
Possible	Replication	Not possible

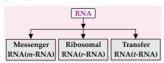
- □ James Watson and Francis Crick gave a double strand helix structure for DNA. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.
- In secondary structure of RNA, helices are present which are only single stranded. Sometimes they fold back on themselves to form a double helix structure.



Chargaff's rule

 Amount of purine bases is always equal to that of pyrimidine bases. Purine base of one strand of DNA molecule pairs with pyrimidine base of the other strand. Adenine (A) pairs with thymine (T) through two H-bonds (A = T) and guanine (G) pairs with cytosine (C) through three H-bonds ($G \equiv C$).

In case of RNA, adenine (A) pairs with uracil (U), (A = U).



Importance

- Replication is the process by which a single DNA molecule produces two identical copies of itself.
- □ Protein synthesis occurs in two steps, i.e., transcription and translation.
 - O Transcription is the process of synthesis of RNA.
 - Translation: The synthesis of proteins occur in the cytoplasm of the cell. The m-RNA directs protein synthesis with the help of r-RNA and t-RNA.
- □ Genetic code : Linear sequences of three nucleotides (triplets) in DNA or RNA that determines the specific amino acid sequence in the synthesis of proteins is called genetic code. It is the biochemical basis of heredity and nearly universal in all organisms.
- ☐ Mutation : Mutation may be defined as a change in nitrogenous base sequence of DNA molecule which leads to the synthesis of proteins with an altered sequence of amino acids. Mutation may cause genetic disorders or diseases.

POLYMERS

- Introduction
- Types, classification, methods of polymerisation. copolymerisation, some important polymers

TIPS TO REMEMBER

 Polymers are very large molecules having high molecular mass (103-107u).

- These are also referred to as macromolecules, which are formed by joining of repeating structural units monomers on a large scale.
- This process of formation of polymers from respective monomers is called polymerisation.
- All polymers are macromolecules but all macromolecules are not polymers.

Types of Polymers

- Depending upon the nature of the monomers.
 - Homopolymer: Polymer made up of only one type of monomer. e.g., Polythene, Polypropylene, PVC, etc.

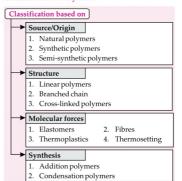
$$nCH_2 = CH_2 \xrightarrow{Polymerisation} + CH_2 - CH_2 +_n$$
Ethene
Polythene

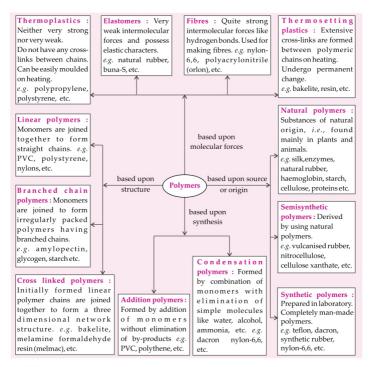
- Copolymer: Polymer made up of two or more types of monomers. e.g., Nylon 6,6, Buna-S, Bakelite, etc. The process of formation of copolymer is called copolymerisation.
 - Copolymers have better physical and mechanical properties. The properties of copolymers could be changed by varying the amount of each monomer.



Nylon 6, 6

Classification of Polymers





Methods of Polymerisation

Addition or chain growth polymerisation

- In this type of polymerisation reactions, monomers are unsaturated compounds.
- Leads to an increase in chain growth through the formation of either free radical or ionic species (cation or anion).
- Depending upon the reactive particles formed in this method of polymerisation, it is further divided into three types.
 - (i) Free radical polymerisation
 - (ii) Cationic polymerisation
 - (iii) Anionic polymerisation

(i) Free radical polymerisation:

It takes place in three steps:

 Chain initiating step: This step requires initiators which are free radicals produced on heating. e.g. benzoyl peroxide, acetyl peroxide, dioxygen, etc.

$$\begin{array}{c} \bigcap\limits_{R-C-O}\bigcap\limits_{CO-C-R}\bigcap\limits_{A\rightarrow 2R-C-O\rightarrow 2R+2CO_2}\bigcap\limits_{R+CH_2-CH_2\rightarrow R-CH_2-CH_2}\bigcap\limits_{A\rightarrow 2R+2CO_2}\bigcap\limits_{A\rightarrow 2CO_2}\bigcap\limits_{A\rightarrow 2C$$

 Chain propagating step: The free radical thus formed adds to the double bond of the monomer to form larger free radical.

$$R-CH_{2}-\dot{C}H_{2} \xrightarrow{CH_{2}=CH_{2}} \\ \sqrt{R-CH_{2}-CH_{2}-CH_{2}-\dot{C}H_{2}} \\ R+CH_{2}-CH_{2}-\dot{h}_{1}CH_{2}-\dot{C}H_{2}$$

- O Chain terminating step : The growing free radical chain consumes free radicals either by combination or by disproportionation to get polymer.
 - Combination $2R + CH_2 - CH_2 + CH_2 - \dot{C}H_2$

 $R + CH_2CH_2 + CH_2CH_2CH_2 + CH_2CH_2 + CH_2CH_2 + R$

- Disproportionation

$$R + CH_2 - CH_2 + CH_2 - CH_2$$

$$R + CH_2 - CH_2 + CH_2 - CH_2$$
Alkene
$$R + CH_2 - CH_2 + CH_2 - CH_3$$
Alkane

- (ii) Mechanism of cationic addition polymerisation: Initiated by the use of strong Lewis acids such
 - as HF, AlCl₃, H₂SO₄, etc. $H_2SO_4 \longrightarrow H^+ + HSO_4$

 $H^+ + CH_2 = CH_2 \longrightarrow CH_3 - CH_2^+$

e.g. polyvinyl ether, polyisobutylene, polystyrene, etc.

(iii) Mechanism of anionic addition polymerisation: Initiated by strong bases such as NaNH2, C4H9Li and Grignard reagent, etc.

$$B: + CH_2 = CH_2 \longrightarrow B - CH_2 - CH_2^-$$

e.g. polyacrylonitrile, polyvinyl chloride and polymethyl methacrylate, etc.

Condensation or step growth polymerisation: In this type of polymerisation reactions, monomers are bifunctional and form bond with the loss of simple molecule of water, alcohol, ammonia, etc. The dimer formed, also contain two functional groups, thus undergo a series of condensations in a stepwise manner and results in the formation of a high molecular mass condensation polymer.

Preparation of Some Important Addition Homopolymers

Polyolefins

Polymer	Structure of monomer	Structure of polymer
Polythene	CH ₂ = CH ₂ Ethylene	-(CH ₂ -CH ₂) _n
Polypropylene	CH ₃ —CH = CH ₂ Propylene	$\begin{pmatrix} CH_3 \\ -CH - CH_2 \end{pmatrix}_n$ $\begin{pmatrix} CF_2 - CF_2 \end{pmatrix}_n$
Polytetrafluoroethene (Teflon) (PTFE)	$CF_2 = CF_2$ Tetrafluoroethene	$+(CF_2-CF_2)_n$
Polyacrylonitrile (Orlon) (PAN)	CH ₂ = CHCN Acrylonitrile (Vinyl cyanide)	$\begin{pmatrix} \text{CN} \\ \text{I} \\ \text{CH}_2 - \text{CH} \end{pmatrix}_n$
Polyvinyl chloride (PVC)	CH ₂ = CHCl Chloroethene (Vinyl chloride)	$ \begin{array}{c} CI \\ CH_2-CH_{f_1} \end{array} $ $ \begin{array}{c} CH_2-CH_{f_2} \end{array} $
Polystyrene (Styron)	CH ₂ =CH	$\begin{bmatrix} CH_2 - CH \end{bmatrix}_n$
Polymethylmethacrylate (PMMA)	CH ₃ CH ₂ =C-COOCH ₃ Methylmethacrylate	$\begin{pmatrix} H_3C \\ CH_2-C \\ J_n \\ COOCH_3 \end{pmatrix}$

Polymonochlorotrifluoroethylene (PCTFE)	Cl-C=CF ₂ F Chlorotrifluoroethylene	$\begin{pmatrix} C1 \\ C - CF_2 \\ F \end{pmatrix}_n$
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Polydienes

Polymer	Structure of monomer	Structure of polymer
Natural rubber	CH ₃ CH ₂ =C-CH=CH ₂ Isoprene (2-Methyl-1, 3-butadiene)	$\begin{pmatrix} \text{CH}_3 \\ \text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2 \end{pmatrix}_n$ <i>cis-</i> 1, 4-Polyisoprene
Neoprene (synthetic rubber)	CI I CH ₂ =C-CH=CH ₂ Chloroprene (2-Chloro-1, 3-butadiene)	$\begin{pmatrix} CI \\ I \\ CH_2 - C = CH - CH_2 \end{pmatrix}_n$
Gutta-percha	CH ₃ CH ₂ =C-CH=CH ₂ Isoprene (2-Methyl-1, 3-butadiene)	CH_3 $CH_2-C=CH-CH_2$ $trans-Polyisoprene$

Preparation of Some Important Addition Copolymers

Polydienes

Polymer	Structure of monomer	Structure of polymer
Buna-S (Styrene Butadiene Rubber) (SBR)	$CH_2 = CH - CH = CH_2$ 1, 3-Butadiene $CH = CH_2$ $Styrene$	+CH ₂ -CH=CH-CH ₂ -CH-CH ₂) _n
Buna-N (Nitrile rubber)	CH ₂ =CH-CH=CH ₂ 1,3-Butadiene CH ₂ =CH-CN Acrylonitrile	CN +CH ₂ -CH=CH-CH ₂ -CH ₂ -CH+

Preparation of Some Important Condensation Homopolymers

Polyamides

Polymer	Structure of monomer	Structure of polymer
Nylon-6 (Perlon-L)	H ₂ C CH ₂ H ₂ C CH ₂ Caprolactam	$ \begin{pmatrix} O & H \\ II & I \\ -C - (CH_2)_5 - N_{f_n} \end{pmatrix} $

Polyesters

Polymer	Structure of monomer	Structure of polymer
Polyhydroxy butyrate (PHB)	OH CH ₃ -CH-CH ₂ -COOH 3-Hydroxybutanoic acid	$ \left\{ \begin{array}{c} O - CH - CH_2 - C \\ CH_3 \end{array} \right\}_n $

Preparation of Some Important Condensation Copolymer

Polyamides

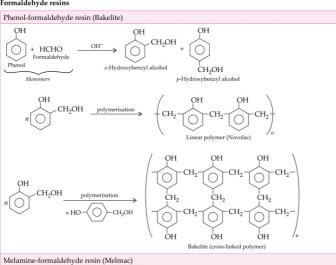
Polymer	Structure of monomer	Structure of polymer
Nylon-6,6	$HOOC-(CH_2)_4-COOH$ $Adipic acid$ $H_2N-(CH_2)_6-NH_2$ $Hexamethylenediamine$	$ \begin{pmatrix} H & H & O & O \\ I & I & II & II \\ +N-(CH_2)_6-N-C-(CH_2)_4-C \\ f_{rr} \end{pmatrix} $
Nylon-6, 10	HOOC—(CH ₂) ₈ —COOH Sebacic acid H ₂ N—(CH ₂) ₆ —NH ₂ Hexamethylenediamine	$ \begin{pmatrix} H & H & O & O \\ I & I & II & II \\ +N-(CH_2)_6-N-C-(CH_2)_8-C \\ \end{pmatrix}_n $
Nylon-2, 6	H ₂ N - CH ₂ - COOH Glycine H ₂ N - (CH ₂) ₅ - COOH 6-Aminohexanoic acid	$ \begin{pmatrix} H & O & H & O \\ I & II & I & II \\ -N-CH_2-C-N-(CH_2)_5-C \\ \end{pmatrix}_{\!$

Polyesters

Polymer	Structure of monomer	Structure of polymer
Terylene (Dacron)	HOCH2—CH2OH Ethylene glycol (Ethane-1.2-diol) HOOC——————————————————————————————————	ФСН ₂ СН ₂ —О—С——————————————————————————————————
Glyptal (Alkyd resin)	HOCH2 – CH2OH Ethylene glycol COOH COOH Phthalia caid (Benzene-1,2-dicarboxylic acid)	$ \left\{ \begin{array}{ccc} OCH_2CH_2-O-C & O & O \\ OCH_2CH_2-O-C & O \\ OCH_2CH_2-O-C & O \\ OCH_2CH_2-O-C & O \\ OCH_2$

Poly β-hydroxy butyrate-co-β-hydroxy valeratre (PHBV)	OH CH ₃ -CH-CH ₂ -COOH 3-Hydroxybutanoic acid OH CH ₃ -CH ₂ -CH-CH ₂ -COOH 3-Hydroxypentanoic acid	$ \begin{array}{c c} & & & & & & & & & & \\ & & & & & & & & $
Poly(glycolic acid) poly(lactic acid) (Dextron)	HO-CH ₂ -COOH Glycolic acid CH ₃ 1 HO-CH-COOH Lactic acid	O-CH ₂ -C-O-CH-C O CH ₃ O) _n

Formaldehyde resins

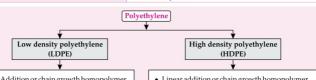


$$\begin{array}{c} H_2N \xrightarrow{6} \stackrel{1}{N} \xrightarrow{2} NH_2 \\ \downarrow M_2 \\ NH_2 \\ NH_2 \\ Melamine \\ (2.4, 6-Triamino-1,3,5-triazine) \\ \end{array} \begin{array}{c} H_2N \xrightarrow{N} \stackrel{N}{N} NHCH_2OH \\ NH_2 \\ NH_2 \\ NH_2 \\ NH_3 \\ NH_4 \\ NH_2 \\ NH_2 \\ NH_3 \\ NH_4 \\ NH_5 \\ NH_6 \\ NH_7 \\ NH_8 \\ NH_9 \\ N$$

Urea-formaldehyde resin $NH_2CONH_2 + HCHO \longrightarrow +NH-CO-NH-CH_2+$ Urea Formaldehyde Urea-formaldehyde resin Monomers

Polysulphide

Thiokol Cl-CH2CH2-Cl Ethylene dichloride +CH2CH2-S-S-S-S+. Na₂S₄ Sodium tetrasulphide



- Addition or chain growth homopolymer.
- · By heating ethylene under high pressure (1000-2000 atm) at temperature of 350-570 K in presence of traces of oxygen or peroxide.
- · Free radical addition polymerisation.
- · Highly branched polymer.
- · Low density (0.92 g/cm3), low melting point (384 K)
- · Transparent, moderate tensile strength.
- · Chemically inert, tough but flexible.
- · Used for packaging, insulation and manufacturing squeeze bottles, pipes, tovs, etc.

- Linear addition or chain growth homopolymer.
- · By heating ethylene at 333-343 K and 6-7 atm in presence of Ziegler-Natta catalyst.
- · Coordination polymerisation
- Linear molecules, closely packed.
- · High density (0.97 g/cm3), high melting point (403 K).
- Translucent
- · Chemically inert, quite harder, greater tensile strength.
- · Used for manufacturing containers, housewares and pipes, etc.

RUBBER

It is an example of elastomer.

Natural rubber

- It is obtained from latex of rubber tree.
- O It is also known as cis-1,4-polyisoprene (about 5,000 units).

- O It is a linear 1, 4-addition polymer.
- O It is elastic as the intermolecular forces present are weak van der waals' forces.
- O The cis configuration gives the polymeric chain of natural rubber a coiled structure, it can be stretched by the application of forces

- and returns back to original coiled shape when forces are removed.
- Gutta-percha: All trans configuration occurs naturally as Gutta-percha.

- It is also known as trans-polyisoprene.
- It is non-elastic and non-crystalline.

Synthetic rubber

It is obtained by polymerizing certain organic compounds which may have properties similar to rubber and some additional desirable properties. Most of these polymers are derived from butadiene derivatives. These are also vulcanized. For example, neoprene, styrene butadiene rubber (SBR), thiokol, silicones, polyurethane rubber.



GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Mode of occurrence of elements

Native State

Elements with very low reactivity occur in free state. e.g. C, S, N, noble gases, metals like Ag, Au, Pt, etc.

Combined State

- Minerals: Elements which are very reactive, occur in the form of their compounds called minerals (metals exist in oxidised form, non-metals exist in reduced form).
- Ores: The minerals from which metals can be conveniently and economically extracted are called ores. For example, Bauxite (Al₂O₂xH₂O), Haematite (Fe₂O₂), Magnetite (Fe₂O₄), Malachite [CuCO₃Cu(OH)₂], Sphalerite (ZnS), Cuprite (Cu₂O), Siderite (FeCO₃), Iron pyrites (FeS₂), Copper pyrites (CuFeS₂),

Extraction and Isolation of metals from ores

Step - 1

Crushing and Grinding (Pulverisation) of the Ore

○ Lumps of ore Crushers Small pieces Ball pieces Fine powder

Sten - 3

Isolation of Crude Metals

It involves two steps:

/Conversion of the Ore into Metal oxide /

Two methods are used based upon the nature of the ores.

 Calcination: Carbonates and hydrated oxide ores heated strongly in a limited supply of air or in the absence of size

$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$
Limonite Ferric oxide

 $CuCO_3$. $Cu(OH)_2 \xrightarrow{\Delta} 2CuO + CO_2 \uparrow + H_2O$ Malachite Copper(II) oxide

Malachite Copper(II) oxide

Roasting: Sulphide ores strongly heated in excess of air.

2PbS + 3O₂ → 2PbO + 2SO₂↑

Lead sulphide Lead oxide

Both the processes are carried out in reverberatory furnace.

Reduction of the Metal oxide to the Free metal

By carbon: Smelting.

 By heating with a suitable reducing agent called thermal reduction or pyrometallurgy.

e.g., oxides of less reactive elements like Fe, Cu, Zn, Cr, Sn, Mn, etc.

 Reduction by Al: Aluminothermy or Goldschmidt thermite process.

 $Fe_2O_3+2A1 \xrightarrow{\Delta} Al_2O_3+Fe$

 Autoreduction: For reduction of sulphide ores of Pb, Hg and Cu. No reducing agent used.

 $2Cu_2S+3O_2 \longrightarrow 2Cu_2O+2SO_2$ $2Cu_2O+Cu_2S \longrightarrow 6Cu+SO_2$

 Electrometallurgy: By electrolysis of highly electropositive metals like group 1 and 2, Al, etc.

e.g., Down's process: Na is obtained by electrolysis of fused NaCl.

Hall and Heroult process: Al is obtained by electrolysis of a

mixture of fused purified alumina and cryolite.

O Reduction by precipitation: Hydrometallurgy or

displacement method.

e.g., Ag and Au

4Ag+8 NaCN+O₂+2H₂O

4Na[Ag(CN)]

 $4Ag+8NaCN+O_2+2H_2O \longrightarrow 4Na[Ag(CN)_2]+4NaOH$ $2Na[Ag(CN)_3]+Zn \longrightarrow Na_3[Zn(CN)_4]+2Ag\downarrow$

Step - 2

Concentration of the Ore

Removal of unwanted materials i.e., gangue or matrix from the ore is called ore-dressing or benefaction of ore. The important methods are

- Hand picking.
- Gravity separation or levigation or hydraulic washing: For oxide ores, based on difference in densities of ore (heavier) and gangue particles. e.g. haematite, tinstone, etc.
- Magnetic separation: Based on difference in magnetic properties.
 e.g. chromite (FeO.Cr₂O₃), magnetite (Fe₃O₄) and pyrolusite (MnO₂) being magnetic are separated from non-magnetic siliceous gangue.
- Froth floatation: This method is based on preferential wetting of ore (by oil) and gangue (by water). e.g. sulphide ores such as zinc blende (ZnS), copper pyrites (CuFeS₂), galena (PbS), etc.
- Chemical method Leaching: When ore is soluble in a suitable solvents. Baeyer's process: For Al → from bauxite.

Mac Arthur-Forrest cyanide process: For Ag and $Au \rightarrow from their native ores$

Step - 4

Purification or Refining of the Crude Metal

Extracted metal is contaminated with some impurity.

- Distillation: The impure metal is evaporated to obtain pure metal as distillate. For low boiling points metals. e.g. Zn, Hg, Cd, etc.
- Liquation: Low melting metal gets separated from high melting impurities by making it flow on a sloping surface. For low melting points metals. e.g. Sn, Pb, Bi, etc.
- Electrolytic refining:
 - Impure metal → anode
 - Pure metal → cathode
 - Solution of a soluble salt of metal → electrolytic solution
 - On passing electricity, insoluble impurities settle down below anode as anode mud or anode sludge.
 - e.g., Cu, Ag, Au, Pb, Ni, Cr, Zn, Al, etc.
- Zone refining: To obtain very high purity metals, e.g. Si, Ge, B, Ga, In, As, etc. based on principle of fractional crystallization i.e., difference in solubilities of impurities in molten and in solid state of metal.
- Vapour phase refining: Metal is converted to its volatile compound which is then decomposed to give pure metal.
 - Mond process for refining Ni:

Ni(CO)₄ 450-470 K ➤ Ni+4CO

van Arkel method for refining Zr or Ti:
 Zr + 2I₂ 870 K ZrI₄

- Poling: When impurities of own metal present. e.g. Cu₂O in blister copper and SnO₂ in crude tin.
- Cupellation: When impurities of other metals present form volatile oxides. e.g. Pb traces in Ag.

- Neoprene rubber: It is prepared by polymerization of chloroprene. Neoprene is superior to natural rubber in its stability to aerial oxidation and its resistance to solvents.
- Styrene Butadiene Rubber (SBR) or Buna-S: Polymer of buta-1, 3-diene and styrene. It is very tough and is a good substitute for natural rubber.
- Nitrile rubber (Buna-N): Polymer of 1,3-butadiene and acrylonitrile. Resistant to the action of petrol, lubricating oils and organic solvents, etc.
- Thiokol: Copolymer of ethylene dichloride and sodium polysulphide. It has slightly less tensile strength than natural rubber but is exceptionally resistant to chemicals.
- Vulcanisation of rubber: It is heated with sulphur at a temperature of 373-415 K. Process of heating natural rubber with sulphur to improve its properties is called vulcanisation. Cross-links make rubber hard, tough with greater absorption tendency, resistant to oxidation and organic solvents. Sulphur forms cross-links at reactive sites. The extent of stiffness of vulcanised rubber depends upon the amount of sulphur added.

Kev Points

- PHBV, poly(glycolic acid) poly(lactic acid) and nylon-2-nylon-6 are biodegradable polymers.
- Biodegradable polymers are useful for medical goods, for controlled drug release and in agriculture materials.

CHEMISTRY IN EVERYDAY LIFE

- Introduction
- Chemicals in medicines
- Chemicals in food
- Cleansing agents

TIPS TO REMEMBER

- In various areas, chemicals are used as
 - medicines for the treatment of diseases.
 - food materials
 - cleansing agents like soaps, detergents, household bleaches, tooth pastes, etc.
 - synthetic fibres made up of chemicals only.

CHEMICALS IN MEDICINES

- Drugs are the chemicals of low molecular masses (-100-500 u) which interact with macromolecular targets and produce a therapeutic and useful biological response. These chemicals are called medicines.
- Use of chemicals for therapeutic effect is called chemotherapy.
- Classification of drugs: Drugs are classified on the basis of

Drug action

- It is based on the action of a drug on a particular biochemical process.
- · Antihistamines

Pharmacological effect

- Analgesics (pain killer)
- Antiseptics (kill or arrest the growth of microorganisms)
- microorganiono)
- Antipyretics (reduce fever)

Chemical structure

- It is based on the chemical structure of the drug.
- Sulphonamides

Molecular targets

DRUGS

 It is based on the interaction with biomolecules such as carbohydrates, lipids, proteins and nucleic acids.

Therapeutic Action of Drugs

- Antacids: Drugs which reduce or neutralise acidity. These drugs raise the pH of stomach to some appropriate level. Baking soda, metal hydroxides like Al(OH)₃, Mg(OH)₂, cimetidine, ranitidine, lansoprazole, omeprazole are few examples of antacids.
- 1 Antihistamines (anti-allergic drugs): Drugs which interfere with the natural action of histamine by competing with histamine for binding sites of receptor and therefore diminish its effect.
 - Histamines are the chemicals released by most cells during on allergic reaction.

- Diphenylhydramine (Benadryl), pheniramine maleate (avil), chlorpheniramine (zeet) are few examples of antihistamines.
- Neurologically active drugs: Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.
- Tranquilizer: It is a class of chemical compounds used for the treatment of stress, mild and severe mental diseases. These are commonly called psychotherapeutic drugs. These are the essential component of sleeping pills. Some examples according to the action of drugs are:
 - O Narcotics: It reduces anxiety and tension. e.g., heroin, pethidine, etc.
 - O Sedatives: It reduces the action of central nervous system. e.g., valium, barbiturates.
 - Antidepressants (mood boosters) reduce depression, e.g., iproniazid, phenelzine, etc.
 - Chlordiazepoxide and meprobamate, are relatively mild tranquilizers suitable for relieving tension. Equanil is used in controlling depression and hypertension.
 - Hypnotics (sleep producing Barbiturates such as seconal, luminal, veronal
 - Non-hypnotic drugs: Valium and serotonin.
- □ Analgesics : Drugs which relieve pain without causing impairment of consciousness, mental confusion, paralysis.
 - O Non-narcotic: Drugs which do not cause addiction. e.g., aspirin, paracetamol are analgesics as well as antipyretics. Aspirin is also used in prevention of heart attack due to its anticlotting property.
 - Narcotics: Their chronic use leads to addiction. e.g. morphine, codeine, etc.
- Antimicrobial: Human beings and animals are prone to diseases caused by action of microorganisms such as bacteria, fungi, virus and other pathogens.
 - Drugs which inhibit the action or growth of these microbes are antimicrobial.
 - O Antibiotics, antiseptics and disinfectants are
- Antibiotics: These are the chemicals synthesised from microbes and have either cidal (killing) [Bactericidal] effect or a static (inhibitory) [Bacteriostatic] effect on microbes.

antimicrobial drugs.

- Depending upon the range of microorganisms affected; antibiotics are classified as broad spectrum antibiotics and narrow spectrum antibiotics
 - Antibiotics which kill or inhibit a wide range of Gram-positive and Gramnegative bacteria are said to be broad spectrum antibiotics. Those effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics.
 - e.g. penicillin (a bactericidal and narrow spectrum antibiotic), ampicillin and amoxicillin (semisynthetic modifications of penicillin), ofloxacin (broad spectrum),
 - e.g.erythromycin,tetracycline,chloramphenicol (a bacteriostatic and broad spectrum antibiotic), etc.
- Antiseptics: These are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
 - Examples are furacine, soframicine, dettol (a mixture of chloroxylenol and terpineol), 0.2% solution of phenol.
 - Bithionol (also called bithional) is added to soaps, iodine, iodoform, etc.
- □ Disinfectants : These substances kill or stop the growth of micro-organisms, but are harmful to living cells as well. So used on non-living objects like clothes, floors, utensils, etc. e.g. phenol, bleaching powder, H2O2, etc.
- 1% solution of phenol is used as disinfectant. Antifertility drugs: These drugs are used to reduce birth rates. e.g. mifepristone, silphium,

CHEMICALS IN FOOD

- Chemicals which are added to food for their preservation or enhancing their appeal, flavour, etc. are known as food additives.
- □ Artificial sweetening agents : These are the compounds which give sweetening effect and enhance colour and flavour of food.
 - e.g. saccharin, aspartame, alitame, etc.

Artificial sweetener	Sweetness value in comparison to cane sugar
Sodium cyclamate	30-50
Aspartame	100
Dulcin	250
Saccharin	550
Sucralose	600
Alitame	2000

- □ Food preservatives: These are the chemical substances which are added to the food materials to prevent their spoilage and to retain their nutritive value for long periods. These preservatives prevent the rancidity of food and inhibit the growth or kill the micro-organisms, e.g. table salt, sugar, citric acid, sodium benzoate, salts of propionic acid, sorbic acid, etc.
- Antioxidants: These are the chemical substances which prevent oxidation and subsequent spoilage of the food. These act as sacrificial materials, i.e. they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the ageing process. e.g., Butylated hydroxy anisole (BHA) and butylated hydroxy toluene (BHT).

Kev Point

Artificial sweetening agents are inert and harmless thus excreted from the body in urine unchanged. Use of artificial sweetners is of great value to diabetic persons and people who need to control intake of calories.

CLEANSING AGENTS

- Soaps: These are sodium or potassium salts of higher fatty acids (with 16-18 carbon atoms). e.g. Salts of C₁₅H₃₁COOH (palmitic acid), C₁₇H₃₅COOH (stearic acid), C₁₇H₃₅COOH (oleic acid), C₁₇H₃₁COOH (linoleic acid), etc.
 - Soaps containing sodium salts are prepared by heating glyceryl ester of fatty acid with aqueous NaOH solution and the reaction is known as saponification.
 - Only Na/K soaps are soluble in water and are used for cleaning purposes. Generally potassium soaps are soft to the skin than sodium soaps.

Key Points

- Soaps do not work in hard water.
- Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.
- These insoluble soaps separate as scum in water and are useless as cleansing agent.
- Synthetic detergents: Also called as soapless soaps, as they have all the properties of soaps, but actually do not contain any soap.

- Used with both soft and hard water.
- Chemically, these are sodium salts of long chain sulphonates and sulphates.
- These are classified as:
 - Cationic detergents: Their polar head is positively charged.
 - e.g. cetyltrimethylammonium bromide CH₃(CH₂)₁₅N⁺(CH₃)₃Br⁻
 - These are used as fabric softner and hair conditioner.
 - Anionic detergents: Their polar head is negatively charged.

$$e.g., CH_3-(CH_2)_{10}-CH_2-O-S-\bar{O}Na^+$$

sodium lauryl sulphate

Such detergents are used to wash clothes.

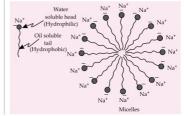
 Non-ionic detergents: Their polar head is neutral. e.g. Polyethylene glycol stearate, CH₃(CH₂)₁₆COO(CH₂CH₂O)_nCH₂CH₂OH Such detergents are used in dish washers.

Advantages of Synthetic Detergents over Soaps

- They can be used in hard water, in acidic medium while soaps get precipitated.
- They are more soluble in water and thus form lather more easily.
- They are stronger cleansing agents than soaps as they decrease the surface tension to greater extent.

Cleansing Action of Soaps and Detergents

□ In the micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere. Because they are negatively charged, soap micelles repel each other and remain dispersed in water.



Questions for Practice

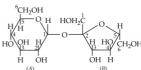


- (a) Glucose, Sucrose
- (b) Glucose, Fructose
- (c) Hexanal, Acetophenone
- (d) Fructose, Sucrose
- 2. A peptide made up of n number of amino acids contains how many peptide linkages?
 - (b) n+1 (c) 2n-1 (d) n-1
- 3. The pyrimidine base, common in both DNA and RNA is
 - (a) Thymine
- (b) Cytosine
- (c) Guanine
- (d) Uracil
- HOCH₂ OOH 4. In the structure, an anomeric carbon is HO
 - (a) 1 (b) 2 (c) 3 (d) 4
- 5. Tocopherol is the chemical name of vitamin (a) K (b) E (c) H (d) D
- 6. In DNA, the complementary bases are
 - (a) adenine and guanine; thymine and cytosine
 - (b) uracil and adenine; cytosine and guanine
 - (c) adenine and thymine; guanine and cytosine
 - (d) adenine and thymine; guanine and uracil.
- 7. Which of the following sets contain only addition
 - homopolymers? (a) Polythene, Natural rubber, Cellulose

 - (b) Nylon, Polyester, Melamine resin
 - (c) Teflon, Bakelite, Orlon
 - (d) Neoprene, PVC, Polythene
- 8. Which of the following is an example of nonbiodegradable detergent?
 - (a) CH₃--(CH₂)₁₁-

 - CH₂ (c) CH₃-(CH-CH₂)₃-CH
 - (d) CH₃-(CH₂)₁₀-CH₂OSO₃Na

- 9. Phenacetin is used as a/an
 - (a) antipyretic (b) antiseptic
 - (c) antimalarial (d) disinfectant.
- 10. Which of the statements about "Denaturation" given below are correct?
 - (1) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
 - (2) Denaturation leads to the conversion of double strand of DNA into single strand.
 - (3) Denaturation affects primary structure which gets distorted.
 - (a) (2) and (3) (b) (1) and (3)
 - (c) (1) and (2) (d) (1), (2) and (3)
- 11. Observe the given disaccharide and choose the correct statement.



- (a) Ring (B) is furanose with β-glycosidic link.
- (b) Ring (A) is furanose with α-glycosidic link.
- (c) Ring (A) is pyranose with α-glycosidic link.
- (d) Both (a) and (c).
- In nucleic acid, base is linked to __ pentose sugar and phosphoric acid is attached to _____ of a pentose sugar.
 - (a) C-5, C-2 (b) C-2, C-5
 - (c) C-1, C-5 (d) C-5, C-1
- 13. Vitamin which is neither water soluble nor fat soluble is
 - (b) B₁₂ (c) H (a) K
- 14. Which of the following sets of polymers contain biodegradable polymers?
 - (a) PHBV, Nylon-2,6, PGA, PLA
 - (b) PHBV, Nylon-6,10, PVC, PLA
 - (c) PMMA, Nylon-6,6, PGA, PVC
 - (d) Both (b) and (c).
- 15. Match the list I with list II and select the correct answer using the code given below the lists.

List II

- P. Neutral amino acid Arginine
- O. Acidic amino acid 2. Aspartic acid
- R. Basic amino acid Valine

- 2) 1 2 3
- (a) 1 2 3 (b) 2 1 3
- (c) 1 3 2
- (c) 1 3 2 (d) 3 2 1
- 16. Which of the following is not correctly matched?

(a) Neoprene:
$$\begin{bmatrix} CH_2 - C = CH - CH_2 \end{bmatrix}_n$$

(b) Nylon-6, 6:

$$\begin{bmatrix} V_{1} & V_{2} & V_{3} & V_{4} & V_{5} & V$$

(c) Terylene:
$$\left\{OCH_2-CH_2-C\right\}$$

d) PMMA:
$$\{CH_2 - C\}_n$$

- A sulpha drug used for the treatment of pneumonia is
 - (a) sulpha acetamide(b) sulphaguanidine(c) sulphanilamide(d) sulphapyridine.
- 18. Among cellulose, polyvinyl chloride, nylon and natural rubber, the polymer in which the
 - intermolecular force of attraction is weakest is
 (a) nylon (b) polyvinyl chloride
 - (c) cellulose
- (b) polyvinyl chloride(d) natural rubber.
- Match the list I with list II and select the correct answer using the code given below the lists.

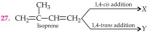
List I List II P. Alkylbenzene 1. Antioxidants

- sulphonate
 Q. Sodium oleate
 2. Detergent
- R. Sodium benzoate 3. Soap
- S. Butylated hydroxy 4. Food preservatives toluene (BHT)
 - PQRS
- (a) 1 2 3 4 (b) 4 3 2 1
- (c) 2 3 1 4
- (c) 2 3 1 4 (d) 2 3 4 1
- 20. Identify the correct statement.
 - (a) The starting material for the manufacture of PVC is obtained by reacting HCl with acetylene.
 - (b) Natural rubber is a step growth polymer.
 - (c) Dacron is addition polymer.
 - (d) Intermolecular forces present in nylon-6,6 is H-bonding.

- 21. Which is the correct statement about birth control pills?
 - (a) Contain estrogen only
 - (b) Contain progesterone only
 - (c) Contain a mixture of estrogen and progesterone derivatives
 - (d) Progesterone enhances ovulation.
- Match the list I with list II and select the correct answer using the code given below the lists.

P. Phenol + Formaldehyde 1. Saran Q. Terephthalic acid 2. Bakelite

- + Ethylene glycol R. Caprolactam 3. Nylon-6
- S. Vinyl chloride + Vinylidine 4. Terylene chloride
 - PQRS
- (a) 1 2 3 4 (b) 4 2 2 1
- (c) 2 4 3 1
- (d) 2 4 1 3
- 23. Which of the following is added to soaps for transparency?
 - (a) Benzene
- (b) Ethyl chloride
- (c) Ethanol (d) Barbituric acid
- The chemical name for melamine is
 (a) 1.3.5-triamino-2.4.6-triazine
 - (b) 2,4,6-triamino-1,3,5-triazine
 - (c) 2-amino-1,3,5-triazine
 - (d) 2,4-diamino-1,3,5-triazine.
- Barbituric acid and its derivatives are well known as
 - (a) tranquilizers (b) antiseptics
 - (c) analgesics (d) antipyretics.
- The first step in bakelite formation is
 (a) aromatic nucleophilic substitution
 - (b) aromatic electrophilic substitution
 - (c) condensation
 - (d) electrophilic addition.



X and Y are respectively

- (a) natural rubber, gutta percha
- (b) gutta percha, natural rubber
- (c) natural rubber, natural rubber
- (d) gutta percha, gutta percha

- 28. The bactericidal and bacteriostatic antibiotics respectively are
 - (a) penicillin, ofloxacin
 - (b) erythromycin, tetracycline
 - (c) penicillin, chloramphenicol
 - (d) tetracycline and penicillin
- 29. The compound that causes general antidepressant action on the central nervous system belongs to the class of
 - (a) analgesics
- (b) tranquilizers
- (c) narcotic analgesics (d) antihistamines.
- Hexamethylenediamine

Adipic acid Sebacic acid

Polymers X and Y are respectively

- (a) nylon-6; nylon-6, 6 (b) nylon-6, 6; nylon-6
- (c) nylon-6; nylon-6, 10 (d) nylon-6, 6; nylon-6, 10

SOLUTIONS

- (b) (d) (b) (a) (c) : DNA contains two types of nitrogenous
- Purine: Adenine (A) and Guanine (G) Pyrimidine: Cytosine (C) and Thymine (T)
- Adenine pairs with thymine (A = T) by two hydrogen bonds and guanine with cytosine $(G \equiv C)$ by three hydrogen bonds. 7. (d): Neoprene is made from chloroprene, PVC
- from vinyl chloride and polyethene from ethene monomers.
- 8. (c): Greater the branching, greater is the nonbiodegradability.
- (c): Denaturation does not change the primary structure of protein.
- 11. (d): Ring (A) is pyranose with α-glycosidic linkage while ring (B) is furanose with β -glycosidic linkage.
- 12. (c) 13. (c) 14. (a)

(c): Terylene contains ester linkage, i.e. -OCH2-CH2-O-CO-

- 17. (d)
- 18. (d): Cellulose and nylon are fibres and thus their intermolecular forces are the strongest. Polyvinyl chloride is a thermoplastic, the intermolecular forces in them are neither strong nor weak. Natural rubber has weak van der Waals forces, which are the weakest forces.
- 19. (d)
- 21. (c): Birth control pills contain a mixture of estrogen and progesterone derivatives.
- 22. (c)
- 23. (c): For transparency, ethanol is added to soaps.

25. (a): The most commonly used tranquilizers are barbituric acid and its 5, 5-disubstituted derivatives such as veronal, luminal and seconal.

They polymerise to give bakelite

- 27. (a): 1.4-cis addition reaction of isoprene gives natural rubber while 1,4-trans addition reaction of isoprene gives gutta percha.
- 28. (c) 29. (b)
- 30. (d): nNH_2 —(CH₂)₆—NH₂+nHOOC—(CH₂)₄—COOH Hexamethylenediamine 1 -2nH2O Adipic acid +CO-NH-(CH₂)₆-NH-CO-(CH₃)₄-CO+, Nylon-6,6
 - nNH_2 — $(CH_2)_6$ — NH_2 +nHOOC— $(CH_2)_8$ —COOH-2 nH₂O Sebacic acid Hexamethylenediamine

+CO(CH₂)₈CO-NH(CH₂)₆NH-CO(CH₂)₈-CO+ Nylon-6, 10

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry. This year JEE (Main & Advanced) / NEET / AIIMS / other PMTs have drawn their papers heavily from NCERT books Practise hard ! All the best !!

1.	Rearrange the following (I to IV) in the order of	ĺ
	increasing masses and choose the correct answer.	П

- 1 atom of oxygen
- (II) 1 atom of nitrogen
- (III) 1×10^{-10} g molecular mass of oxygen (IV) 1×10^{-7} g atomic mass of copper.
- (a) II < I < III < IV
- (b) IV < III < II < I
- (c) II < III < I < IV
- (d) III < IV < I < II
- 2. An electron of mass 9.1 × 10⁻²⁸ g is moving with a velocity of 3.0×10^4 cm s⁻¹, accurate upto 0.011%. The uncertainty in its position is
 - (a) 0.125 cm (c) 0.175 cm
- (b) 0.556 cm (d) 0.756 cm
- 3. Elements P, Q, R and S have atomic numbers 12,
 - 19, 29 and 36 respectively. To which group of the periodic table, element P,
 - Q, R and S belong? (a) 1, 2, 18, 11 (c) 2, 1, 14, 16
- (b) 13, 15, 17, 18 (d) 2, 1, 11, 18
- 4. Which of the following pairs consists of species with same bond order?
 - (a) C2, O2 (b) N2, O2
 - (c) B2, F2
- (d) Both (a) and (c).
- Two bulbs A and B of equal capacity are filled with He and SO₂ respectively at the same temperature. If the pressure in the two bulbs is same, then the ratio of the velocities of the molecules of two gases will be
 - (a) 6 (c) 2
- (b) 4 (d) 1
- 6. In the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be

[Given: $\Delta G_{\ell}^{\circ}(N_2O_4) = 100 \text{ kJ}; \Delta G_{\ell}^{\circ}(NO_2) = 50 \text{ kJ}$] The reaction will be in

- (a) forward direction (b) reverse direction (c) equilibrium
 - (d) cannot say.

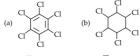
- Consider the following reactions.
 - $X_{(g)} + 3Y_{(g)} \rightleftharpoons XY_{3(g)}; \Delta H = -50.2 \text{ kJ mol}^{-1}$ The reaction will proceed in the forward direction
 - (a) high temperature and low pressure
 - (b) low temperature and low pressure (c) high temperature and high pressure
 - (d) low temperature and high pressure.
 - The degree of hardness of a sample of water containing 6 mg of MgSO4 per kg of water (in ppm) is
 - (a) 4 (b) 2 (c) 6 (d) 5
- 9. Lattice energies of BeF2, MgF2, CaF2 and BaF2 are - 2906, - 2610, - 2459 and - 2367 kJ molrespectively. Hydration energies of Be2+, Mg2+, Ca2+, Ba2+ and F are - 2494, - 1921, - 1577, - 1305 and - 457 kI mol-1 respectively. Which of the following fluorides is soluble in water?
 - (a) BeF₂
- (b) MgF₂
- (c) CaF₂
- (d) BaF₂
- In an oxidation process for a cell, M₁ → M₁ⁿ⁺ + ne⁻ the other metal (M_2) being univalent showing reduction takes up electrons to complete redox reaction.
 - (a) (n-1)
- (b) 1 (d) 2
- (c) n
- 11. Which of the following is electron deficient compound?
 - (a) C₂H₆ (c) PH₃
- (b) SiH₄
- (d) B₄H₁₀
- 12. The IUPAC name of the given compound is



- (a) 2,4,4-trimethylhex-5-ene-5-ol
- (b) 3,3,4,4-tetramethylbut-1-en-2-ol (c) 3,3,5-trimethylhex-1-en-2-ol
- (d) none of the above.

13. Identify the product Z of the following reaction.

$$\xrightarrow{UV/500 \text{ K}} Z$$





- 14. The process of 'eutrophication' is due to
 - (a) increase in concentration of insecticide in water
 - (b) increase in concentration of fluoride ion in
 - (c) the reduction in concentration of the dissolved oxygen in water due to phosphate pollution
 - (d) attack of younger leaves of a plant by peroxyacetyl nitrate
- 15. Potassium has a bcc structure with nearest neighbour distance 4.52 Å. Its atomic weight is 39. Its density will be
 - (a) 454 kg m⁻³ (c) 852 kg m⁻³
- (b) 804 kg m⁻³ (d) 910 kg m⁻³
- 16. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g benzene is lowered by 0.45°C. The degree of association of acetic acid in benzene is [Assume acetic acid dimerises in benzene, K_t for benzene = $5.12 \text{ K kg mol}^{-1}$
 - (a) 94.5% (c) 68.4%
- (b) 98.7%
- (d) 33.4%
- 17. The equilibrium constant K, for the reaction $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)'} (E^{\circ}_{cell} = 0.46 \text{ V})$

 - (a) antilog 15.6 (b) antilog 2.5
 - (c) antilog 1.5
- (d) antilog 12.2
- 18. The rate constant for the first order decomposition of a certain reaction is described by the equation $\log(k) = 14.34 - \frac{1.25 \times 10^4}{1.25 \times 10^4}$

At what temperature will its half-life period be 256 minutes?

- (a) 338 K
- (b) 570 K
- (c) 490 K
- (d) 669 K

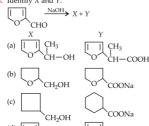
- 19. Plot of $\log x/m$ against $\log P$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be ($\log 5 = 0.6990$)
 - (a) 1 g (c) 3 g
- (b) 2 g (d) 5 g
- 20. In the extraction of nickel by Mond's process, the metal is obtained by
 - (a) electrochemical reduction
 - (b) thermal decomposition
 - (c) chemical reduction by aluminium
 - (d) reduction by carbon.
- 21. The number of P-O-P bridges in the structure of phosphorus pentoxide and phosphorus trioxide are respectively
 - (a) 5, 5
- (b) 6, 5
- (c) 5, 6
- (d) 6.6
- 22. The number of d-electrons in Fe^{2+} is not equal to that of the
 - (a) p-electrons in Cl⁻(b) s-electrons in Fe³⁺
 - (c) s-electrons in Mg(d) v-electrons in Ne
- 23. When one mole of each of the following complex salts is treated with excess of AgNO3, which of them gives maximum amount of AgCl?
 - (a) [Co(NH₃)₆]Cl₃
- (b) [Co(NH₃)₅Cl]Cl₂
- (c) [Co(NH₃)₄Cl₂]Cl (d) Na₂[PtCl₆]

24.
$$C_7H_8 \xrightarrow{3Cl_2/\Delta} P \xrightarrow{Br_2/Fe} Q \xrightarrow{Zn/HCl} R$$

The compound R is

- (a) o-bromotoluene
- (b) m-bromotoluene
- (c) v-bromotoluene
- (d) 3-bromo-2, 2, 6-trichlorotoluene
- 25. Which one among C₄H_oOH will be optically active?
 - (a) Butan-1-ol
- (b) Butan-2-ol
- (c) 2-Methylpropan-1-ol
- (d) 2-Methylpropan-2-ol
- 26. The increasing order of boiling points of the following compounds is
 - 1, 2-dihydroxybenzene
 - (II) 1, 3-dihydroxybenzene
 - (III) 1, 4-dihydroxybenzene
 - (a) II < I < III (b) I < III < II
 - (c) I < II < III (d) III < II < I
- 27. The common name of the following compound is CH₃-CH-CH-CHO CI CH₃

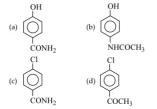
- (a) 2-chloro-3-methylbutan-4-al
- (b) α-chloro-β-methylbutyraldehyde
- (c) β-chloro-α-methylbutyraldehyde
- (d) Both (a) and (c).
- 28. Identify X and Y.



29. Phenol

In the above reaction sequence, P, Q and R are respectively

- (a) benzene, nitrobenzene, aniline
- (b) benzene, m-dinitrobenzene, m-nitroaniline
- (c) toluene, m-nitrotoluene, m-toluidine
- (d) benzene, nitrobenzene, hydrazobenzene.
- 30. Which of the following amides will not undergo Hofmann bromamide reaction?
 - (a) CH2CONH2 (c) C₆H₅CONH₂
- (b) CH₂CH₂CONH₂ (d) CH2CONHCH2
- 31. If one strand of DNA has the sequence ATGCTTGA, the sequence in the complimentary strand would be
 - (a) TACGAACT
- (b) TCCGAACT
- (c) TACGTACT
- (d) TACGTAGT
- 32. The correct structure of the drug paracetamol is



- 33. Orlon is a polymer of
 - (a) Styrene
- (b) Tetrafluoroethylene
- (c) Vinyl chloride
- (d) Acrylonitrile
- 34. Among KO₂, AlO₂, BaO₂ and NO₂, unpaired electron is present in
 - (a) NO₂⁺ and BaO₂
- (b) KO2 and AlO2
- (c) KO2 only
- (d) BaO2 only
- 35. Which of the halide does not exist?
 - (a) TICl
- (b) PbBr₄
- (c) PbCl₂ (d) SnCl₂ 36. For which of the following compounds Lassaigne's
- test of nitrogen will fail? (a) H₂NCONH.NH₂.HCl
 - (b) H₂NNH₂.2HCl
 - (c) H₂NCONH₂
 - (d) C₆H₅-N=N-C₆H₅
- 37. Both Co3+ and Pt4+ have a coordination number of six. Which of the following pairs of complexes will show approximately the same electrical conductance for their 0.001 M aqueous solutions?
 - (a) CoCl₃·4NH₃ and PtCl₄·4NH₃ (b) CoCl₃·3NH₃ and PtCl₄·5NH₃

 - (c) CoCl₃·6NH₃ and PtCl₄·5NH₂
 - (d) CoCl₃·6NH₃ and PtCl₄·3NH₃
- 38. Which of the following arrangements represent increasing oxidation number of the central atom?
 - (a) CrO₂, ClO₃, CrO₄², MnO₄
 - (b) ClO₃, CrO₄², MnO₄, CrO₇²
 - (c) CrO₂⁻, ClO₃⁻, MnO₄⁻, CrO₄²
 - (d) CrO₄², MnO₄, CrO₂, ClO₂
- 39. 0.759 g of a silver salt of a dibasic organic acid on ignition left 0.463 g metallic silver. The equivalent weight of acid is
 - (a) 70.0
- (b) 108
- (c) 60
- (d) 50
- 40. A monoatomic anion of unit charge contains 45 neutrons and 36 electrons. Identify the ion.
 - (a) Cl-
- (b) F
- (c) I (d) Br
- 41. A dibasic acid containing C, H and O was found to contain C = 26.7% and H = 2.2%. The vapour density of diethyl ester was found to be 73. What is molecular formula of acid?
 - (a) CH2O2
- (b) C₂H₂O₄
- (c) C₃H₃O₄
- (d) C₄H₄O₄

 The pressure of O₂ (in atm) over a sample of NiO at 25°C if ΔG° = 212 kJ for the reaction

$$NiO_{(s)} \rightleftharpoons Ni_{(s)} + \frac{1}{2}O_{2(g)}$$
 is

- (a) 4.9×10^{-25} atm (b) 5.02×10^{-25} atm (c) 4.9×10^{-75} atm (d) 5.02×10^{-75} atm

- 43. A solution contains Pb2+ and Fe2+ ions. To it some quantity of Fe and Pb is added.

$$[E_{E_0^{2+}/E_0}^{\circ} = -0.44 \text{ V}, E_{Ph^{2+}/Ph}^{\circ} = -0.126 \text{ V}]$$

- (a) concentration of Pb2+ ions will remain unaffected
- (b) concentration of Pb2+ ions will increase
- (c) concentration of Fe2+ ions will increase
- (d) concentration of Fe2+ ions will decrease.
- 44. Initial concentration of A is 0.25 (M), the parallel path is given as;

$$5A \xrightarrow{k_1 \to B} B$$
 is

where $k_1 = 1.5 \times 10^{-5} \text{ s}^{-1}$ and $k_2 = 5 \times 10^{-6} \text{ s}^{-1}$ Find the value of concentration of C after 5 h of reaction (parallel).

- (a) $7.56 \times 10^{-2} \,\text{M}$ (b) $7.56 \times 10^{-3} \,\text{M}$ (c) $0.756 \,\text{M}$ (d) $7.56 \times 10^{-4} \,\text{M}$
- 45. A hydrocarbon (C₆H₁₂) on ozonolysis gives ethanal and 2-methylpropanal.

On the basis of ozonolysis product, the structure of hydrocarbon is

- (c) CH₃-CH₂-CH=CH-CH₂-CH₃
- (d) CH₃-CH=CH-CH-CH₃ CH₃
- The statement true for N₃ is
 - (a) it has a non-linear structure
 - (b) it is called interhalogen
 - (c) the formal oxidation state of nitrogen in this anion is -2
 - (d) it is isoelectronic with NO2.
- **47.** In a first-order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is

- 48. Allyl chloride on dehydrochlorination gives
 - (a) propadiene
 - (b) propylene
 - (c) allyl alcohol
- (d) acetone.
- 49. The change in optical rotation with time of freshly prepared solution of reducing sugar is known as
 - (a) inversion
- (b) specific rotation
- (c) rotatory motion (d) mutarotation.
- 50. Identify the least stable ion amongst the following.
 - (a) Li
- (b) Be-
- (c) B
- (d) C

SOLUTIONS

- 1. (a): (I) Mass of one O atom = $\frac{10}{6.023 \times 10^{23}}$ $= 2.66 \times 10^{-23} g$
 - (II) Mass of one N atom = 6.023×10²³ $= 2.32 \times 10^{-23} g$
 - (III) 1 g-molecule of oxygen = 32 g 1×10^{-10} g-molecule of oxygen = 32×10^{-10} $= 3.2 \times 10^{-9} \text{ g}$
 - (IV) 1 g-atom of copper = 63 g 1×10^{-7} g-atom of copper = 63×10^{-7} $= 6.3 \times 10^{-6} \text{ g}$

Therefore, the increasing order of masses are II < I < III < IV

2. (c): According to Heisenberg's principle

We know that $\Delta x \times m\Delta v = \frac{h}{4\pi}$ Given, $\Delta v = 3 \times 10^4 \times \frac{0.011}{100} = 3.3 \text{ cm s}^{-1}$

On substituting the value of
$$\Delta v$$
,
$$\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.63 \times 10^{-27}}{4 \times 3.14 \times 9.1 \times 10^{-28} \times 3.3}$$

3. (d):

Element	At. no.	Electronic configuration	Group
P	12	$1s^2 2s^2 2p^6 3s^2$	2
Q	19	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^1$	1
R	29	$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^{10} \ 4s^1$	11
S	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ $4s^2 4p^6$	18

- (d): M.O. electronic configuration of C₂ is: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$
 - ∴ B.O. = $\frac{8-4}{2}$ = 2

M.O. electronic configuration of N2 is: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_v)^2 (\pi 2p_v)^2 (\sigma 2p_v)^2$

$$\therefore B.O. = \frac{10-4}{2} = 3$$

M.O. electronic configuration of B2 is: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2v_*)^1 (\pi 2v_*)^1$

$$\therefore$$
 B.O. = $\frac{6-4}{2}$ = 1

M.O. electronic configuration of O2 is: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$

$$\therefore B.O. = \frac{10-6}{2} = 2$$

M.O. electronic configuration of F2 is: $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_y)^2 (\pi^* 2p_y)^2$

$$\therefore B.O. = \frac{10-8}{2} = 1$$

5. (b): Let the velocities of He and SO₂ be c_1 and c_2 respectively.

$$c_1 = \sqrt{\frac{3RT}{M_{He}}} \text{ and } c_2 = \sqrt{\frac{3RT}{M_{SO_2}}}$$

$$\frac{c_1}{c_2} = \sqrt{\frac{M_{SO_2}}{M_{He}}} = \sqrt{\frac{64}{4}} = 4$$

6. (b): Standard Gibbs free energy change for the reaction, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$\Delta G^{\circ} = \Delta G^{\circ}_{\text{products}} - \Delta G^{\circ}_{\text{reactants}}$$

$$= 2 \times 50 - 100 = 0$$

$$\Delta G^{\circ} = -2.303 \ RT \log K_{0} = 0; K_{0} = 1$$

Initially,
$$P_{N_2O_4} = P_{NO_2} = 10$$
 bar

Initially,
$$P_{\text{N2O}_4} = P_{\text{NO}_2} = 10 \text{ bar}$$

So, $Q_{P \text{ (initial)}} = \frac{(P_{\text{NO}_2})^2}{P_{\text{N2O}_4}} = 10$

Initial Gibbs free energy of the above reaction,

$$\Delta G = \Delta G^{\circ} + 2.303 \ RT \log Q_{p}$$

 $\Delta G = 0 + 2.303 \times 8.314 \times 298 \log 10$
 $= 5.705 \times 10^{3} \text{ kJ mol}^{-1}$

Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.

- 7. (d): For an exothermic process, decrease in temperature and increase in pressure will favour the forward reaction with decrease in volume or number of moles.
- 8. (d): 1 g-mol or 120 g MgSO₄ = 1 g-mol

$$6 \times 10^{-3} \text{ g MgSO}_4 = \frac{100 \times 6 \times 10^{-3}}{120}$$

= $5 \times 10^{-3} \text{ g of CaCO}_3$

Thus, 1000 g of water contains MgSO₄ equivalent to 5×10^{-3} g of CaCO₃

So, 10^6 g of water will contain = $\frac{5 \times 10^{-3}}{1000} \times 10^6$ = 5 g of CaCO₃

:. Hardness of given water sample = 5 ppm

9. (d): BeF₂:

Hydration energy =
$$-2494 + 2 \times (-457)$$

= -3408

Lattice energy = -2906

$$\Delta H_{\text{solution}} = -3408 - (-2906)$$

= -502 kJ mol⁻¹

 MgF_2 :

Hydration energy =
$$-1921 + 2 \times (-457)$$

= -2835

Lattice energy = -2610

$$\Delta H_{\text{solution}} = -2835 - (-2610)$$

= -225 kJ mol⁻¹

CaF2:

Hydration energy =
$$-1577 + 2 \times (-457)$$

= -2491

Lattice energy = -2459

$$\Delta H_{\text{solution}} = -2491 - (-2459)$$

= -32 kJ mol⁻¹

Hydration energy =
$$-1305 + 2 \times (-457)$$

= -2219

Lattice energy = - 2367

$$\Delta H_{\text{solution}} = -2219 - (-2367)$$

= + 148 kJ mol⁻¹

 $\Delta H_{\text{solution}}$ is +ve in BaF₂, hence BaF₂ is easily soluble in water.

10. (c): The reaction shows $M_2^{n+} + ne^- \rightarrow M_2$ i.e., electrons released at anode = electrons used at cathode

11. (d)

3,3,5-Trimethylhex-1-en-2-ol

13. (b): Under ultraviolet light, three chlorine molecules add to benzene ring to produce benzene hexachloride, C6H6Cl6, also known as gammaxane.

- 14. (c): Eutrophication is the term given to enrichment of water bodies by plant nutrients. It is the process by which lakes are enriched naturally or more usually by human activity. The key nutrients responsible for eutrophication are nitrogen and phosphorus.
- prosprious. 15. (d): For bcc, $d = \frac{\sqrt{3}}{2}a$ or $a = \frac{2d}{\sqrt{3}} = \frac{2 \times 4.52}{1.732} = 5.219 \text{ Å} = 522 \text{ pm}$ Density $= \frac{Z \times M}{a^3 \times N_A}$ $= \frac{2 \times 39}{(522)^3 \times (6.023 \times 10^{23}) \times 10^{-30}}$ $= 0.91 \text{ g/cm}^3 = 910 \text{ kg m}^{-3}$
- 16. (a): Given: w = 0.2 g, W = 20 g, $\Delta T = 0.45$ °C Applying, $\Delta T_f = \frac{1000 \times K_f \times w}{M \times W}$

or
$$0.45 = \frac{1000 \times 5.12 \times 0.2}{M \times 20}$$

 $2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2$ Before association 1 0 After association 1 - α $\alpha/2$ (mol. wt. acetic acid = 60)

$$\therefore \frac{M_{\text{(normal)}}}{M_{\text{(observed)}}} = 1 - \alpha + \frac{\alpha}{2} \text{ or } \frac{60}{113.78} = 1 - \alpha + \frac{\alpha}{2}$$

- $\alpha = 0.945 \text{ or } 94.5\%$
- 17. (a): $E^{\circ} = \frac{0.059}{n} \log K_c$ $0.46 = \frac{0.059}{n} \log K_c$ $\frac{0.46 \times 2}{0.059} = \log K_c$
 - $\Rightarrow \log K_c = 15.59$
 - $K_c \approx \text{antilog } 15.6$
- 18. (d): Since the reaction is of first order,

$$t_{1/2} = \frac{0.693}{k}$$
or $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \cdot 60} = 4.51 \cdot 10^{-5} \text{ s}^{-1}$

Substituting this value in the given expression, we get

$$\log (4.51 \ 10^{-5}) = 14.34 - \frac{1.25 \ 10^4}{T}$$
or
$$-4.346 = 14.34 - \frac{1.25 \ 10^4}{T}$$

or
$$\frac{1.25 \cdot 10^4}{T} = 14.34 + 4.346 = 18.686$$

or
$$T = \frac{1.25 \cdot 10^4}{18.686} = 669 \text{ K}$$

19. (d): According to Freundlich equation $\frac{x}{y} = kP^{1/n} \quad \text{or } \log \frac{x}{y} = \log k + \frac{1}{n} \log P$

.. Plot of
$$\log x/m \ vs \log P$$
 is linear with slope
= $1/n$ and intercept = $\log k$.

Thus $\frac{1}{n} = \tan \theta = \tan 45^\circ = 1$ or n = 1At P = 0.5 atm and k = 10 $\frac{x}{n} = 10 \times (0.5)^1 = 5$ $\therefore x = 5$ g

(b): In extraction of nickel by Mond's process, metal is obtained by thermal decomposition.

Ni + 4CO
$$\xrightarrow{57 - 77^{\circ}C}$$
 Ni(CO)₄
Ni(CO)₄ $\xrightarrow{177^{\circ} - 197^{\circ}C}$ Ni + 4CO

- 22. (a): $CI^- = 1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ $Fe^{2+} = 1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^6$ In Fe^{2+} , total number of d-electrons = 6

which is not equal to p-electrons in Cl^- (i.e., 12).

23. (a): When [Co(NH₃)₆|Cl₃ is treated with excess of AgNO₃ then 3 moles of AgCl are obtained, as there are 3 ionisable ions in the complex (present outside the coordination sphere). The presence of ionisable CT ions are responsible for the formation of AgCl. Compounds (b) and (c) have two and one ionisable CT ions respectively, whereas (d) has none. Thus complex (a) gives maximum amount of AgCl.

4. (b):
$$\bigcirc \bigcap_{3\text{Cl}_2 \Delta} \bigcirc \bigcap_{Br_2/Fe} \bigcirc \bigcap_{CCl_3} \bigcirc \bigcap_{Br_2/Fe} \bigcirc \bigcap_{CCl_3} \bigcirc \bigcap_{CCl_3}$$

(b): It is butan-2-ol as it contains chiral carbon atom.

$$H_5C_2$$
 C^*
OH

*C is chiral carbon atom

26. (c): 1,4-dihydroxybenzene shows highest boiling point among given compounds due to intermolecular H-bonding, 1,3-dihydroxybenzene has three dimensional crystalline structure which is more stable due to self-association. 1,2-dihydroxybenzene shows intramolecular H-bonding which is weaker than intermolecular H-bonding. Hence order of their boiling points is 1,2-dihydroxybenzene < 1,3-dihydroxybenzene <

29. (d):
$$C_6H_5OH$$
 \xrightarrow{Zn} C_6H_6 $\xrightarrow{HNO_3+H_2SO_4}$ $\xrightarrow{333 \text{ K}}$ Phenol Benzene (P)

 $C_6H_5NH-NHC_6H_5 \xrightarrow{Zn/NaOH}$ $C_6H_5NO_2$ $\xrightarrow{Hydrazobenzene}$ (R) Nitrobenzene (R)

- (d): Only 1° amides undergo Hofmann bromamide reaction. Since CH₃CONHCH₃ is a 2° amide, therefore, it does not undergo Hofmann bromamide reaction.
- (a): Two strands of DNA are antiparallel and complimentary to each other.
 If one strand has the sequence ATGCTTGA then the sequence in the complimentary strand would be TACGAACT.

- 33. (d): Acrylonitrile
- 34. (c): NO₂ contains three electron bond and in NO₂^{*} odd (unpaired) electron is removed. Peroxides (O₂²) do not possess unpaired electrons as the antibonding \(\text{m} \) M.O.'s acquired one more electron each for pairing. AlO₂^{*} is obtained by

the interaction of Al³+ $(2s^2 2p^6$ configuration) and two oxide (O^2^-) ions each of which does not contain unpaired electrons. Superoxide O_2^- has one unpaired electron in π antibonding M.O. and is therefore paramagnetic.

- 35. (b)
- (b): H₂NNH₂· 2HCl does not contain carbon, hence does not give positive results for Lassaigne's test for nitrogen.
- 37. (c): CoCl₃·6NH₃ and PtCl₄·5NH₃ This pair of complexes will show approximately same electrical conductance for their 0.001 M

$$\begin{aligned} &\text{aqueous solution as} \\ &[Co(NH_3)_6]Cl_3 & [PtCl(NH_3)_5]Cl_3 \\ && \downarrow \text{in solution} \\ &[Co(NH_3)_6]^{3^*} + 3Cl^- & [PtCl(NH_3)_5]^{3^*} + 3Cl^- \end{aligned}$$

As the number of ionic species in solution due to both the complexes are equal. Therefore their equimolar solutions will show approximately same conductance.

 (a): Writing the O.N. of Cr, Cl and Mn on each species in the four set of ions, we have,

(a)
$$CrO_2^-$$
, ClO_3^- , CrO_4^{2-} , MnO_4^-

(b)
$$ClO_3^-$$
, CrO_4^{2-} , MnO_4^- , CrO_2^{-}

(d)
$$\overset{+6}{Cr}O_4^{2-}$$
, $\overset{+7}{Mn}O_4^{-}$, $\overset{+3}{Cr}O_2^{-}$, $\overset{+5}{Cl}O_3^{-}$

Only in arrangement (a) the O.N. of central atom increases from left to right. Therefore option (a) is correct.

39. (a): Equivalent mass of acid

$$= \left(\frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} \times 108\right) - 107$$
$$= \left(\frac{0.759}{0.463} \times 108\right) - 107 = 70.0$$

40. (d): Let the monoatomic anion be X⁻.

Number of electrons in $X^- = 36$

:. Number of electrons in monoatomic atom (X) = 36 - 1 = 35

Atomic number = number of electrons is neutral atom = number of protons in neutral atom = 35 Mass number of monoatomic atom (*X*)

= number of protons + number of neutrons = 35 + 45 = 80

Hence, ion must be Br-.

41 (b) ·

41. (0):				
Element	С	Н	О	
Percentage	26.7	2.2	100 - (26.7 + 2.2) = 71.1	
Atomic mass	12	1	16	
Atomic ratio	$\frac{26.7}{12} = 2.22$	$\frac{2.2}{1}$ = 2.2	$\frac{71.1}{16}$ = 4.44	
Simplest ratio	$\frac{2.22}{2.2} \approx 1$	$\frac{2.2}{2.2} \approx 1$	$\frac{4.44}{2.2} \approx 2$	
Simple whole no. ratio	1	1	2	

Hence empirical formula is CHO2. Empirical formula mass = $12 + 1 + 2 \times 16 = 45$ Molecular mass of diethyl ester = $73 \times 2 = 146$ Molecular mass of acid

= Molecular mass of ester

- 2 × Molecular mass of C₂H₁ +2 × Atomic mass of H

$$n = \frac{146 - 2 \times 29 + 2 = 90}{\text{Molecular mass}} = \frac{90}{45} = 2$$
Empirical formula mass

Molecular formula = (Empirical formula), $= C_2H_2O_4$

42. (c): ΔG° is related to equilibrium constant by $\Delta G^{\circ} = -2.303 RT \log K_n$

and $K_p = \sqrt{p_{O_2}}$ since NiO and Ni are in solid

$$\Delta G^{\circ} = 212 \text{ kJ} = 212000 \text{ J}$$

 $\Delta G^{\circ} = -2.303 RT \log K_{v}$

 \therefore 212000 = -2.303 × 8.314 × 298 log K_n $\log K_n = -37.155$

$$K_p = 7 \times 10^{-38}$$

$$\int p_{O_2} = 7 \times 10^{-38}$$

$$p_{O_2} = 4.9 \times 10^{-75} \text{ atm}$$

43. (c): The reaction that occurs will be $Pb^{2+} + Fe \rightarrow Fe^{2+} + Pb$

> On adding Fe and Pb, Fe will be consumed to increase the concentration of Fe2+.

44. (b):
$$k_{av} = k_1 + k_2 = 20 \times 10^{-6} \,\mathrm{s}^{-1}$$

Also,
$$2.303\log \frac{[A_0]}{[A_1]} = kt$$

or
$$\log \frac{0.25}{[A_t]} = \frac{20 \times 10^{-6} \times 5 \times 60 \times 60}{2.303} = 0.1563$$

or
$$\frac{0.25}{[A_t]} = 1.433$$

$$A_t = \frac{0.25}{1.422} = 0.1744$$

$$\therefore$$
 [A] decomposed = [A₀] - [A_t]
= 0.25 - 0.1744 = 0.0756 M

Fraction of C formed

$$\begin{split} &= \frac{k_2}{k_1 + k_2} \times [A]_{\text{decomposed}} \times \frac{2}{5} \\ &= 0.0756 \times \frac{5 \times 10^{-6}}{20 \times 10^{-6}} \times \frac{2}{5} = 7.56 \times 10^{-3} \,\text{M} \end{split}$$

(c): Azide ion is linear. It is a pseudohalide ion. The formal oxidation state of N in N₃ ion is -2 because in any of the resonating structure, the net charge on the ion is -1.

$$(:\overset{2-}{N}-\overset{+}{N}\equiv N:\longleftrightarrow:N=\overset{+}{N}-\overset{2-}{N}:\longleftrightarrow:N=\overset{+}{N}=\overset{-}{N}:)$$

N₃ has total 22 electrons while NO₂ has 23 electrons.

47. (c): For a 1st order kinetics,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$
At $t_{1/2}$, $k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$
or, $t_{1/2} = \frac{2.303}{k} \log 2 = \frac{\ln 2}{k}$

49. (d)

50. (b): Electronic configuration of Li = 1s², 2s² (all subshells are completely filled, so it is stable). $Be^- = 1s^2$, $2s^2$, $2p^1$ (very much less stable, due to single electron no exchange is possible). $B^- = 1s^2$, $2s^2$, $2p^2$ (less stable, here electron can exchange in one way, thus more stable than Be-) $C^- = 1s^2$, $2s^2$, $2p^3$ (stable due to presence of halffilled 2v-subshell)

2014 CBSE-B@ARD

CHAPTERWISE PRACTICE PAPER

Series-9

Polymers | Chemistry in Everyday Life

Time: 3 hrs. Marks: 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- (ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
- (iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
- (iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
- (v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
- (vi) Use Log Tables, if necessary. Use of calculator is not allowed.
- In nylon 6, 6, what does the designation 6, 6 mean?
- 2. Which site of an enzyme is called allosteric site?
- 3. Name the three antidepressant drugs.
- (i) Name a polymer of glucose which is stored by animals.
 - (ii) Write the commercial name of polyacrylonitrile.
- Is \(\frac{1}{2}\)CH₂\(-\text{CH}(\text{C}_6\)H₅\)\(\frac{1}{n}\) a homopolymer or a copolymer?
- 6. Why is ethanol added to soap?
- Give one example for each of the following:
 - (i) Natural polymer
 - (ii) Chain growth polymer
 - Pick the odd one amongst the following on the basis of their medicinal properties with reason:
 - Chloroxylenol, terpineol, chloramphenicol, bithional.
- 9. Why is molecular mass of polymers always expressed as an average?
- expressed as an average?

 10. (i) What is tincture of iodine? For what purpose
 - (ii) Name the components present in dettol.
- Write the name of monomers of the following polymers.

(ii)
$$-\{C - (CH_2)_5 - N\}_{\overline{n}}$$

OR

Write the name of monomers of the following polymers.

- 12. What is aspirin? Why should it not be taken empty stomach?
- Distinguish between the terms homopolymer and copolymer and given an example of each.
- 14. How are receptor proteins located in the cell membrane?
- What is a biodegradable polymer? Give an example of a biodegradable aliphatic polyester.
- 16. Arrange the following polymers in the increasing order of their intermolecular forces:
 - (i) Nylon 6, 6; Buna-S; polythene
 - (ii) Nylon 6, neoprene, polyvinyl chloride
- 17. Why do we require artificial sweetening agents?

we use it?

- How do antiseptics differ from disinfectants? Give one example of each.
 - Name a compound which can be used as an antiseptic as well as disinfectant.
- Discuss the main purpose of vulcanisation of rubber.
- Describe the following with suitable examples:
 Antioxidants
 - (ii) Artificial sweeteners
 - (iii) Preservatives

OR

Describe the following with suitable examples:

- (i) Antihistamines
- (ii) Antacids
- (iii) Antimicrobials
- 21. Define thermoplastics and thermosetting polymers.
- 22. Karan read an article on water pollution caused by detergents in a science magazine. He at once investigated about the chemicals written on the detergent packet used by her mother for washing clothes. He found that the detergent contained highly branched hydrocarbons. Karan asked his mother to replace the detergent with the one containing hydrocarbons with minimum branching.
 - (i) What values are shown by Karan?
 - (ii) Why Karan asked his mother to change the detergent?
- Explain the differences between polyacrylates and polyesters.
- 24. What are detergents? Give their scheme of classification. Why are detergents preferred over soaps?
- 25. (i) Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem? Name two drugs.
 - (ii) While antacids and antiallergic drugs interfere with the function of histamines, why do these not interfere with the function of each other?
- (i) Write the chemical equation for preparing sodium soap from glyceryl oleate and glyceryl palmitate. Structure of these compounds are given below.
 - (a) (C₁₅H₃₁COO)₃C₃H₅ (Glyceryl palmitate)
 - (b) (C₁₇H₃₃COO)₃C₃H₅ (Glyceryl oleate)
 - (ii) Explain the term target molecules or drug targets as used in medicinal chemistry.

- Could a copolymer be formed in both addition and condensation polymerisation or not? Explain with example.
- (i) What are elastomers? Write the chemical equation to represent the preparation of Buna-S.
 - (ii) Write the information asked for in the following polymers:
 - (a) Bakelite-Materials used for preparation
 - (b) PVC-Monomer unit
 - (c) Synthetic rubber-Monomer unit
 - (d) Nylon-6,6—Materials required for preparation
 - (iii) What is PHBV?

OR

- Comment on the structural difference between thermoplastics and thermosetting polymers.
- (ii) Write the chemical equation representing the synthesis of glyptal. Mention any one of its uses in industry.
- (iii) Explain the term copolymerisation and give two examples.
- 29. (i) Name the action of the following on the human body:
 - (a) Aspirin

(e) Analgin

- (b) Penicillin
- (c) Phenacetin (d) Morphine
 - (f) Luminal
- (g) Seconal (h) Streptomycin
- (ii) Label the hydrophilic and hydrophobic parts in the following compounds.
 - (a) CH₃(CH₂)₁₀CH₂OSO₃Na⁺
 - (b) CH₃(CH₂)₁₅ -N(CH₃)₃Br⁻
 - $\text{(c) } CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$
- Explain the following.
 - (a) Why is the use of aspartame limited to cold foods and drinks?
 - (b) Alitame is high-potency sweetener, it is not used as an artificial sweetener.
 - (c) Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultant with doctor.
- (ii) Why are cimetidine and ranitidine better antacids than sodium hydrogen carbonate or magnesium or aluminium hydroxide?

- 30. (i) How are low density polyethylene and high density polyethylene manufactured? How do they differ in their densities?
 - (ii) How is bakelite made and what is its major use? Why is bakelite a thermosetting polymer?
 - (iii) Give two differences between linear polymers and branched chain polymers. Give one example of each.

OR

- (i) Write the free radical mechanism for polymerisation of ethene.
- (ii) Classify the polymers based on molecular forces between the monomers.
- (iii) Which of the following polymers soften on heating and harden on cooling? What are the polymers with this property collectively called? What are the structural similarities between such polymers?
 - (a) Bakelite
 - (b) Urea-formaldehyde resin
 - (c) Polythene
 - (d) Polyvinyls
 - (e) Polystyrene

SOLUTIONS

- 6,6 means that both the monomers i.e., adipic acid, [(CH₂)₄(COOH)₂] and hexamethylenediamine, [(CH₂)₆(NH₂)₂] of nylon 6, 6 have six carbon atoms.
- Site different from active site of enzyme where a molecule can bind and affect the active site is called allosteric site. Some drugs may also bind at this site.
- 3. (i) Iproniazid (ii) Phenelzine (iii) Equanil
- (i) Glycogen is a polymer of glucose stored by animals.
 - (ii) Commercial name of polyacrylonitrile is orlon (acrilan).

$$nCH_2 = CH - CN \longrightarrow -[CH_2 - CH]_n$$

- It is a homopolymer and the monomer from which it is obtained is styrene C₆H₅CH = CH₂.
- 6. Ethanol is added to soap to make it transparent.
- (i) Natural polymer Natural rubber.
 (ii) Chain growth polymer-PVC (polyvinyl chloride).
- Chloramphenicol. It is antibiotic while all other three are used as antiseptic.

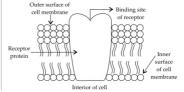
- Growth of the polymer chain depends on the availability of the monomers in the reaction mixture during their synthesis. Thus, the polymer sample contains chains of varying lengths and hence its molecular mass is always expressed as an average.
- 10. (i) Tincture of iodine is 2-3% solution of iodine in ethanol. It is used as an antiseptic.
 - (ii) There are two components in dettol. Their names are chloroxylenol and terpineol.
- (i) H₂N(CH₂)₆NH₂ Hexamethylenediamine HOOC(CH₂)₄COOH – Adipic acid

OK

- (i) $CF_2 = CF_2$ Tetrafluoroethene
- (ii) CH₂ = CH − Cl − Vinyl chloride
- **12.** Aspirin is 2-acetoxybenzoic acid. It is used as an analgesic as well as antipyretic.

It should not be taken empty stomach because it gets hydrolysed to form salicylic acid which causes bleeding in the stomach as well as ulcer formation.

- 13. Homopolymer: Polymers whose repeating structural units are derived from only one type of monomer units are called homopolymers. For example, polythene, PVC, PAN, teflon, polystyrene, nylon 6, etc.
 - Copolymer: Polymers whose repeating structural units are derived from two or more types of monomer molecules are copolymers. For example, Buna-S, Buna-N, nylon 6, 6, polyester, bakelite, etc.
- 14. Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.



- 15. Polymers which disintegrate by themselves over a period of time due to environmental degradation by bacteria, etc. are called biodegradable polymers. For example, PHBV
 - (Poly-β-hydroxybutyrate-co-β-hydroxyvalerate)
- 16. In increasing intermolecular forces
 - Buna-S < Polythene Nylon 6,6 Intermediate Weakest High tensile intermolecular molecular strength forces forces
 - (ii) Neoprene < Polyvinyl chloride < Nylon 6
- 17. Natural sweeteners, e.g.; sucrose add to calorie intake and therefore many people prefer to use artificial sweeteners. Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It appears to be entirely inert and harmless when taken. Its use is of great value to diabetic persons and people who need to control intake of calories.

18.	Antiseptics	Disinfectants	
	These are applied to the living tissues suchas wounds, cuts, ulcers and diseased skin surfaces. Example : Dettol	to inanimate objects such as floors, drains,	

0.2% solution of phenol-antiseptic 1% solution of phenol-disinfectant

- 19. Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperature (< 283 K) and shows high water absorption capacity. It is soluble in non-polar solvents and is nonresistant to attack by oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range between 373 K and 415 K. On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.
- 20. (i) Antioxidants: These are food additives which are added to retard the action of oxygen on the food, thereby help in its preservation. They slow down the ageing process. Example: Butylated hydroxy toluene (BHT) and butylated hydroxy anisole (BHA).

- (ii) Artificial sweeteners : These are the compounds which are added to food to give sweet taste without increasing the calories. Examples: Saccharin, aspartame.
- (iii) Preservatives: These are chemical substances which are added to food to prevent its spoilage due to microbial growth. Example: Sodium benzoate, sorbic acid.

- (i) Antihistamines: Those drugs which counteract the effect of histamine which is produced due to allergy. e.g.; diphenhydramine (benadryl), promethazine.
- (ii) Antacids: Those drugs which are used in treating hyperacidity are called antacids, e.g.; Mg(OH)2, baking soda.
- (iii) Antimicrobials: Those drugs which are used to kill microbes are called antimicrobials, e.g.; erythromycin, penicillin, tetracycline.
- 21. Thermoplastic Polymers: These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Some common thermoplastics are polythene, polystyrene, polyvinyls, etc.
 - Thermosetting Polymers: These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Some common examples are bakelite, urea-formaldehyde resins,
- 22. (i) Environmental concern, awareness and responsible.
 - (ii) Karan asked his mother to change the detergent because bacteria cannot degrade the highly branched hydrocarbon chains. Slow degradation of detergents leads to their accumulation. Effluents containing such detergents reach the ponds, rivers, etc. These persist in water even after sewage treatment and cause foaming in rivers, ponds, etc. and hence water gets polluted.

Polyacrylates		Polyesters	
1.	Addition polymer e.g.; PAN	Condensation polymer e.g.; Terylene	
2.	$\begin{aligned} & \text{Monomer:} \\ & \text{CH}_2 = \text{CH} - \text{CN} \\ & \text{Acrylonitrile} \end{aligned}$	Monomer: HO — CH ₂ — CH ₂ — OH + Ethylene glycol HOOC — COOH Terephthalic acid	
3.	Formed by chain growth polymerisation.	, 10	
4.	They are used for making synthetic fibres and wool.		

- 24. Detergents are the substances which are used along with water for cleaning or removing dirt. Substances other than soaps which have found frequent use as cleansing agents are called synthetic detergents. There are three types of detergents depending on whether large part is positively or negatively charged or neutral (or non-ionic).
 - (i) Cationic detergents: These are mostly chlorides, bromides or acetates of quaternary amines.

(ii) Anionic detergents, e.g.; sodium salts of alkylbenzenesulphonates

CH₃(CH₂)₁₀CH₂OSO₃ Na⁺

sodium laurylsulphate

(iii) Non-ionic detergents are the esters of long chain fatty acids (stearic acid) and polyethylene glycol.

Detergents are preferred over soaps because detergents can be used even in hard water.

25. (i) Iproniazid and Phenelzine are the two drugs which can inhibit enzymes which catalyse the degradation of noradrenaline. This will slow down the metabolism of noradrenaline and will counteract the effect of depression. (ii) Histamine stimulates the secretion of pepsin and hydrochloric acid. The drug antacid or antiallergic prevents the interaction of histamine with the receptors present in the stomach wall which release lesser amount of acid and reduce hyperacidity. Antiallergic and antacid drugs work on different receptors and antiallergic drugs do not affect the secretion of acid in stomach.

- (ii) The biomolecules like carbohydrates, lipids, proteins and nucleic acids which interact with the drug are called target molecules.
- 27. Yes, a copolymer can be formed by both addition and condensation polymerisation like the copolymer of styrene and methylmethacrylate polymerises by additional polymerisation across double bonds.

other examples are SBR, etc.

Whereas the polymerisation of hexamethylene diamine and adipic acid polymerises by condensation polymerisation to give Nylon-6, 6.

- 28. (i) Elastomers: These are polymers in which polymer chains are held together by the weakest intermolecular forces. These can be stretched due to weak forces of attraction.
 - Buns-S can be prepared by reaction of 1,3-butadiene and styrene in presence of sodium as polymerising agent.

$$\begin{array}{c} n \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 + n \text{CH} = \text{CH}_2 \\ 1,3 \text{-Butadiene} & \text{C}_6 \text{H}_5 \\ & \text{Na} & \text{Styrene} \\ & \text{-} \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \\ & \text{C}_6 \text{H}_5 & \text{In} \end{array}$$

- (ii) (a) Phenol and formaldehyde
 - (b) Vinyl chloride
 - (c) Chloroprene
 - (d) Adipic acid and hexamethylenediamine
- (iii) It is poly-β-hydroxybutyrate-co-β-hydroxy valerate. It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which monomer units are connected by ester linkages.

OH
$$CH_{3}-CH-CH_{2}-COOH +$$

$$3-Hydroxybutanoic acid$$
OH
$$CH_{3}-CH_{2}-CH-CH_{2}-COOH$$

$$3-Hydroxypentanoic acid$$

$$CH_{3}-CH-CH_{2}-COOH$$

$$3-Hydroxypentanoic acid$$

$$CH_{3}-CH-CH_{2}-COOH-CH_{2}-COOH$$

$$CH_{3}-CH-CH_{2}-COOH-CH_{2}-COOH$$

$$CH_{3}-CH-CH_{2}-COOH-CH_{2}-COOH$$

$$CH_{3}-CH-CH_{2}-COOH-CH_{2}-COOH$$

$$CH_{3}-CH-CH_{2}-COO$$

The properties of PHBV vary according to the (monomers) ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness 3-hydroxypentanoic acid imparts flexibility to the copolymer.

It is used in speciality packing, orthopaedic devices and even in controlled drug release. When drug is put in a capsule of PHBV, it is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

OR

- (i) Thermoplastics have less intermolecular force of attraction because they are not crosslinked. They become soft on heating and can be remoulded.
 - Thermosetting plastics have strong force of attraction due to cross-linkages. They do not become soft on heating.
- (ii) It is prepared by condensation of ethylene glycol and phthalic acid.

Glyptal is used in making paints and lacquers.

(iii) It is a process in which more than one type of monomers combine together to form copolymer e.g.;

(a)
$$nCH_2 = CH - CH = CH_2 + nCH_2 = CH$$

Buta-1, 3-diene Acrylonitrile

 CN
 CN
 CN
 CN
 CN
 CN
 CN
 CN
 $CH_2 - CH = CH - CH_2 - CH_2 - CH_2$

- 29. (i) (a) Aspirin is an analgesic which is used for relieving pain. It also prevents heart attack.
 - (b) Penicillin is an antibiotic used against large number of infections caused by various cocci, gram-positive bacteria, etc. It is an effective drug for pneumonia. bronchitis, sore throat and abscesses.

- (c) Phenacetin is an antipyretic drug used to bring down temperature of body in high fever.
- (d) Morphine is a strong analgesic. They are narcotics. They cause addiction. They give relief from acute pain, induce sleep and unconsciousness in higher doses.
- (e) Analgin is antipyretic and analgesic. It brings down temperature of body in fever and give relief from pain.
- (f) Luminal produces sleep and is habit forming. These are also called sedative tranquilizers.
- (g) Seconal is an antidepressant (tranquilizer). Sometimes the patients are highly depressed and lose self-confidence. This drug produces feeling of well being and improve efficiency.
- (h) Streptomycin is an antibiotic. It is used to cure tuberculosis.
- (ii) (a) $CH_3(CH_2)_{10}CH_2OSO_3^-Na^+$ Hydrophobic Hydrophilic
- (b) $CH_3(CH_2)_{15} \stackrel{+}{N} (CH_3)_3 Br_-$ Hydrophobic Hydrophilic
- (c) CH₃(CH₂)₁₆COO(CH₂CH₂O)_nCH₂CH₂OH Hydrophobic Hydrophilic

OR

- (i) (a) Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.
 - (b) Sweetness of food cannot be controlled while using alitame as the sweetener as it is about 2000 times sweeter than sucrose. Hence, it is not used.
 - (c) Most of the drugs taken in doses higher than recommended may cause harmful effect and act as poison. Hence, doctor should also be consulted before taking a medicine.
- (ii) Excessive hydrogen carbonate can make the stomach alkaline and trigger the production of even more acid. Metal hydroxides being insoluble do not increase the pH but these can only cure the symptoms and not the cause. While cimetidine and rantitdine drugs prevent the interaction of histamine with the receptors present on the stomach wall which results in release of lesser amount of acid.

 (i) (a) Low density polyethene: It is manufactured by compressing ethene under very high pressure at about 350-570 K in the presence of very small amount of oxygen as catalyst.

as catalyst.

$$nCH_2 = CH_2$$
 $\xrightarrow{O_2 \text{ as catalyst}}$
 $350-570 \text{ K}$,

Ethene

 $1000-2000 \text{ atm}$

Polythene

The polymer consists of branched chains and therefore has low density.

- (b) High density polyethene: It is manufactured by passing ethene under pressure into an inert solvent (aromatic hydrocarbon) containing (C₂H₃)₃Al and TiCl₄ called Ziegler-Natta catalyst. After polymerisation, the catalyst is decomposed by adding dilute acid and the crystalline polymer is filtered off. This polymer consists of almost linear chains and therefore has higher density.
- (ii) Bakelite is prepared by condensation reaction of phenol and formaldehyde. It is used in making electrical switches and switch boards. It is thermosetting polymer because it does not become soft on heating due to cross-linkages.
- (iii) Linear polymers are well packed and have high densities, high tensile strength and also have high melting point, e.g.; high density polythene. Branched chain polymers are irregularly packed and have lower tensile strength and lower melting point than linear polymers, e.g.; low density polythene, These are different from cross-linked polymers because cross-linked polymers are hard, rigid and brittle, e.g.; bakelite.

OR

(i) Chain initiating step

$$\begin{array}{c} 0 & 0 \\ R-C-O \\ \longleftarrow C-R \xrightarrow{\triangle} 2R-C-O \xrightarrow{\longrightarrow} 2R+2CO_2 \end{array}$$

Chain propagating step

Chain terminating step

Combination

$$2R + CH_2 - CH_2 + CH_2 - \dot{C}H_2 \longrightarrow R + CH_2CH_2 + CH$$

- Disproportionation

$$R + \mathsf{CH}_2 - \mathsf{CH}_2 + R + \mathsf{CH}_2 - \mathsf{CH}_2 + \mathsf{CH}_2 + \mathsf{CH}_2 - \mathsf{CH}_2 + \mathsf{CH}_$$

(ii) On the basis of magnitude of intermolecular forces present in the polymers, they are classified into four categories:

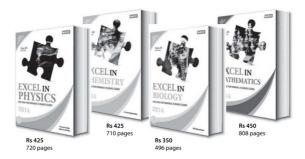
S. No.	Type	Forces between Polymers	Examples
(a)	Elastomers	Polymer chains are held together by the weakest intermolecular forces; being elastic in nature polymer can be stretched. Few crosslinks exist between chains due to which polymer regains its original form after force is released.	Buna-S, Buna-N, Neoprene, $+CH_2-C=CH-CH_2+\pi$ CI
(b)	Fibres	They are thread forming solids with high tensile strength and high modulus. Strong intermolecular forces are due to H-bonding and impart close packing of chains with crystalline structure.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
(c)	Thermoplastic polymers	These are the linear or slightly branched long chain molecules. They have the properties of softening on heating and hardening on cooling. Intermolecular forces of attraction are in between elastomers and fibres.	PVC $+ CH_2 - CH_{7n}$ CI Polythene $+ CH_2 - CH_{2}_{7n}$
(d)	Thermosetting polymers	Intermolecular forces are cross- linked or heavily branched molecules. When heated there occurs extensive cross-linking in moulds and polymer becomes infusible.	Bakelite, urea-formaldehyde resin OH OH CH ₂ Bakelite

(iii) Polythene, polyvinyl and polystyrene soften on heating and harden on cooling. Such polymers are called thermoplastic polymers.

Structural Similarity: They possess intermolecular forces whose strength lies between strength of intermolecular forces of elastomers and fibres.



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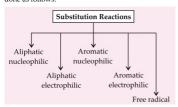


Dear students!! Substitution reaction is an integral part while discussing the reaction mechanism of organic chemistry.

After going through the theory solve the previous engineering/medical questions on this topic. This will help you to apply your concept correctly. This topic and its application will be continued in the next issue. Take care.

*Arunava Sarkar

Chemistry of substitution reactions is quite vast because it has many aspects to study. In general, the first level classification of substitution reactions can be done as follows:



In this issue, main focus will be on aliphatic nucleophilic substitution reactions as other topics will also be discussed in the subsequent chapters.

In general, a nucleophilic substitution reaction can be shown as below:

$$R-X + \ddot{N}u \text{ or } Nu: \longrightarrow R-Nu + \ddot{X}$$

Here, $\hat{N}u$ or $Nu\bar{\imath}$ is the nucleophile. Nucleophile may either be neutral or may be negatively charged. But the nucleophile must have unshared pair of electrons. This is why all nucleophiles are bases *i.e.* Lewis bases. If the nucleophile is a solvent then the reaction may be termed as solvolysis ('lysis' means to 'break down' and here we are breaking the bond between -R and -X by this solvent, if H_2O is used then it is called hydrolysis).

The group which is leaving i.e. \hat{X} is termed as the leaving group (LG) or nucleofuge (the term 'fuge' refers to something that is 'outward' like 'centrifugal

force' is a force which is acting outward from the centre).

Overall, aliphatic nucleophilic substitution can be classified into six categories:

(i)
$$S_N 2$$
 (ii) $S_N 1$ (iii) $S_N i$
(iv) $S_N 1'$ (v) $S_N 2'$ (vi) $S_N i'$

Among these $S_N 2$ and $S_N 1$ mechanisms are common. The above classification has been made based on the substrate, attacking agent. *i.e.* the nucleophile, nucleofuge (the leaving group) and of course a very important factor *i.e.*, the reaction conditions.

S_N2 MECHANISM

The best example to understand S_N^2 mechanism may be the following:

$$\begin{array}{cccc} CH_3Br & + & OH^- & \longrightarrow & CH_3OH & + & Br^- \\ \text{(Substrate)} & \text{(Nucleophile)} & & \text{(Product)} & \text{(Leaving group)} \end{array}$$

S_{8,2} stands for substitution nucleophilic bimolecular. The whole meaning will be cleared gradually. In the above reaction, the nucleophile *i.e.* OH⁻ attacks the carbon atom of methyl bromide from the backside of the leaving group *i.e.* Br⁻; so this is a backside attack. There are two reasons for which backside attack takes place here.

Reason 1: Sterically backside attack is favourable.

Reason 2: Incoming OH⁻ carries negative charge cloud, outgoing Br also carries negative charge cloud. If OH⁻ will attack from the same side of the outgoing Br⁻ there will be severe electrostatic repulsion which will destabilise the system.

$$\begin{array}{c}
H \\
H \\
C \\
\end{array}
\xrightarrow{\delta^+}
\begin{array}{c}
\delta^- \\
Br
\end{array}
\xrightarrow{\delta^-}
\begin{array}{c}
OH
\end{array}$$

Electrostatic repulsion

The process is purely concerted *i.e.* one step process (breaking of —C—Br bond and formation of —C—O bond takes place simultaneously). There is no intermediate (as obvious in case of a concerted process) but there is a single transition state where carbon atom is partially bonded to Br atom and oxygen atom and completely bonded with the three hydrogen atoms (there are very few exceptions where intermediates can be isolated in S_N2 mechanism; to be discussed shortly).

At this stage, hydroxyl group has a decreasing –ve charge and the bromine atom has an increasing –ve charge (because, OH⁻ gives its –ve charge to the carbon atom and the bromine atom starts departing with the shared pair of electrons with carbon). Here,

the energy required to break the C-Br bond is

supplied by the formation of COO bond. At the transition state, carbon atom with its three hydrogen atoms become almost coplanar with the bond angle of 120° (it will be exactly coplanar if the incoming group and the outgoing group will be same, but that is of no practical use).

Useful Concept

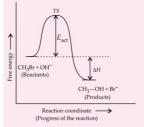
When the transition state appears, the central carbon atom changes its 'hybridisation' state from sp^3 to sp^2 [or tends to a sp^2 hybridisation state]. This is why the bond angles between the central atom carbon and non-interacting atom i.e. hydrogens are 120°. At this stage, one p-orbital becomes almost perpendicular with the plane of the central atom and the non-interacting atoms. One lobe of the p-orbital overlaps with the nucleophile and the other lobe of the p-orbital overlaps with the leaving group. This arrangement ensures the maximum overlap and hence low energy transition state. This is why for S_N2 mechanism it is always the backside attack that takes place; front side attack is not permitted in this case. The credit of the formulation of S_N2 parts goes to Hughes and Ingold.

Energy profile diagram of S_N2

As per the informations given under the point, 'useful concept', the reaction between the hydroxyl ion and the methyl bromide can be shown as below:

As per the RDS, rate = $k[CH_3Br][OH]$

The mechanism is termed as $S_{\rm N}2$ as both the nucleophile (OH) and the substrate are involved in the rate determining step (RDS). The energy profile diagram can be drawn as below:



 $(E_{act} = activation energy and \Delta H = change in enthalpy)$

i.e.
$$\begin{bmatrix} H & H \\ HO & ---C & ---Br \\ H & H \end{bmatrix}$$

Stereochemistry involved in S_N2 mechanism

The nucleophile attacks the carbon atom from the backside of the leaving group. Therefore, initially, if the substrate was chiral then the product obtained will have an inversion of configuration. For example:

$$\begin{array}{c} \text{back} \\ \text{side} \\ \text{slde} \\ \text{slde} \\ \text{H}_5C_2 \\ \text{CH}_3 \\ \text{(R)-(-)-2-bromobutane} \end{array} \\ \begin{array}{c} \text{H} \\ \text{δ-} \\ \text{H}_5C_2 \\ \text{CH}_3 \\ \text{Transition state} \\ \text{Transition state} \\ \text{CH}_3 \\ \text{S-(+)-2-butanol} \\ \text{or} \\ \text{S-(+)-2-butanol} \\ \text{or} \\ \text{S-(+)-butanol} \\ \text{Or} \\ \text{Or} \\ \text{Or} \\ \text{S-(+)-butanol} \\ \text{Or} \\ \text{Or}$$

The approach may be shown using the FMO approach (Frontier Molecular Orbitals refer to 'pericyclic reactions').

A best bonding is offered when there is an overlap between an empty and a filled molecular orbital.

The empty orbital may be considered as LUMO (Lowest Unoccupied Molecular Orbital) whereas the filled molecular orbital is considered as the HOMO (Highest Occupied Molecular Orbital).

Racemisation - an outcome of S_N2 reaction

номо.

Take the last example of the stereochemistry of $S_{N}2$ mechanism.

$$(R)-(-)-2-bromobutane$$

$$H_{5}C_{2}^{(N)}$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$(S)-(+)-2-butanol$$

$$(S)-(+)-2-butanol$$

For each attack one molecule of R-(-)-2-bromobutane is converted into one molecule of S-(+)-2-butanol which is having opposite configuration as well as optical activity with the starting substrate. In a single word, there is an inversion of the configuration which is better known as Walden inversion or Umbrella effect (when you keep your umbrella in the direction

of a strong windflow, the face of the umbrella gets inverted). Now, see that when one molecule of R-(-)-2-bromobutane is converted into one S-(+)-2-butanol then you must observe the following two things:

- Due to inversion, already optical activity of one molecule of R-(-)-2-bromobutane is gone.
- From this R-(-)-2-bromobutane what S-(+)-2-butanol we are getting, will cancel the optical activity of another R-(-)-2-bromobutane.

In this way racemisation is taking place and the most important thing is for inversion of one molecule, there is a cancellation of two molecules. So, rate of racemisation will be twice the rate of inversion. Now, if the optical activity of R-(-)-2-bromobutane and S-(+)-2-butanol are not same then?

Therefore, to better understand we can take radioactive evidence. There is a very common example for it.

In acetone or DMF solvent, when optically active 2-iodooctane reacts with radioactive iodide ion (1²⁸I), then the final alkyl halide is found to contain 1²⁸I and the optical activity of this alkyl halide is zero. So, there is 100% racemisation and a 50% backside attack can generate this racemisation.

(as already explained that rate of racemisation is twice the rate of inversion).

The reaction is found to follow second order kinetics.

$$\begin{array}{c} \operatorname{CH}_3(\operatorname{CH}_2)_5\operatorname{CHI} + ^{128}\operatorname{I}^- \longrightarrow \operatorname{CH}_3(\operatorname{CH}_2)_5\operatorname{CHI}^{128} + \operatorname{I}^- \\ \operatorname{CH}_3 \\ \operatorname{Rate} = k \begin{bmatrix} \operatorname{CH}_3(\operatorname{CH}_2)_5\operatorname{CHI} \\ \operatorname{CH}_3 \end{bmatrix} \begin{bmatrix} 128\operatorname{I}^- \end{bmatrix} \\ \begin{array}{c} \operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \begin{bmatrix} \operatorname{CH}_2)_5\operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \begin{bmatrix} \operatorname{CH}_2)_5\operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \begin{bmatrix} \operatorname{CH}_2)_5\operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \\ \begin{array}{c} \operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \\ \operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \\ \begin{array}{c} \operatorname{CH}_3 \\ \operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \\ \operatorname{CH}_3 \\ \operatorname{CH}_3 \\ \operatorname{CH}_3 \end{bmatrix} \\ \operatorname{CH}_3 \\ \operatorname{CH}_$$

optical activity.

S_N1 MECHANISM

 $\rm S_N 1$ stands for substitution nucleophilic unimolecular. Here, the rate of the reaction depends on the substrate only (say alkyl halide). In general, we can show it as:

$$R - G + \ddot{N}u \longrightarrow R - Nu + \ddot{G}$$

where, rate = $k[R - G]$

The rate of the reaction does not depend on the fact that how much concentration of the nucleophile is involved in the reaction. Basically, the reaction follows a two-step path:

Step-1:
$$R - G \xrightarrow{\text{slow}} R^+ + \ddot{G}$$

$$\longrightarrow \text{Intermediate carbocation}$$
Step-2: $R^+ + \ddot{\tilde{N}}u \xrightarrow{\text{fast}} R - Nu$

As the first step is slow ionization of the substrate, the presence of high dielectric constant containing solvent (e.g. H₂O) is quite necessary. Solvent, preferably should be polar protic as it will help to ease the release of the leaving group and this will promote the ionization of the substrate.

Basically, it has been found that a polar protic solvent forms hydrogen bonding (evidences say that two solvent molecules are involved in it) with the partially negative charge containing leaving group and smoothes its departure from the front side.

Now, as "ionization requires energy; so S_N1 should be an endothermic process ($\Delta H > 0$) and thus unfavourable - then how does it take place"?

Basically, the amount of energy required to ionise R - G is more than compensated by solvation of R^+ and G^-

Take the following example to understand and analyse the different aspects of $S_{\rm N}1$ mechanism:

$$\begin{array}{c} H_3C \\ H_3C \\ H_3C \\ \end{array} \qquad \begin{array}{c} C \\ H_3C \\ \end{array} \qquad \begin{array}{c} C \\ CH_3 \\ \end{array} \qquad \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \qquad \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \qquad \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \qquad \begin{array}{c} CH_3 \\ CH_4 \\ CH_5 \\ C$$

The above reaction, as depicted in the general equation, will occur in two steps:

At this step, the tetrahedral substrate i.e. the tert-butyl bromide undergoes slow ionization to generate a trigonal planar carbocation where the carbon atom bearing the positive charge is sp^2 hybridised. This carbon atom and the atoms connected to it lie on the same plane and the empty pure p-orbital becomes perpendicular to it.

Step-2: At this stage, the nucleophile (i.e. OH) attacks the carbocation to generate the final product i.e. the alcohol. But from which side the nucleophile will attack the carbocation? As the intermediate (i.e. the carbocation) is planar hence its both sides are available to the approaching nucleophile - one is the front side and the another one is backside.

Both the attacks are stereochemically feasible and it generates the mixture of two products where the 50% of the products is with the retention of configuration and another 50% is with the inversion of configuration to the original substrate. Retention is the outcome of front side attack and inversion is the outcome of backside attack.

50% inversion (when overall product is concerned.)

50% retention (when overall product is concerned.)

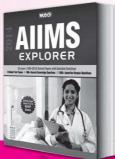
An optically active substrate will finally give a racemic mixture.

$$\begin{array}{c} CH_3 \\ H_5C_2 \\ (CH_3)_3 \\ C \\ H_5C_2 \\ (CH_3)_3 \\ C \\ H_5C_2 \\ (CCH_3)_3 \\ C \\ (CCH_3)_3 \\ (CCH_3)_3 \\ (CCH_3)_3 \\ (CCH_3)_3 \\ (CCH_3)_3 \\ (CCCH_3)_3 \\ ($$

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Organic Chemistry

Mukul C. Ray, Odisha

In the last article, we had discussed the oxidationreduction reactions with special reference to aldehydes and ketones. In continuation to our effort to differentiate between conceptual and informative part of organic chemistry. We present carboxylic acids and their derivatives this time.

 Starting with acidity of carboxylic acids, you can see some comparisons, as the followings are purely conceptual.

- O The electronegativity of $-NO_2$ group is higher than the electronegativity of -F group. But when it comes to a trend of the type shown below, then acidity of carboxylic acids follows the order: α , α , α -trichloroacetic acid > α , α -dichloroacetic acid > α -nitroacetic acid > 2-chlorobutanoic acid > α -iodoacetic acid > 4-chlorobutanoic acid > acetic acid
- The rich chemistry of carboxylic acids is because of so many possible sites for reaction.

 Besides the usual reactions of carboxylic acids with bases like (C₂H₃)₃N, NaOH and reagents like PCl₃, PCl₃, SOCl₂ take close look at the following two reactions, which are generally asked.

$$\begin{array}{c} O \\ II \\ CH_3-C-OH \xrightarrow{H_3\hat{O}^{18}} & CH_3-C-O^{18}H \\ H_2O^{18} & \text{Labelled 'O' appears} \\ \text{at both positions} \end{array}$$

Carboxylates are good nucleophiles.

O Can be easily generated using a base.

$$R - C - O^{2} + Br - CH_{2} - C - O$$

$$R - C - O - CH_{2} - C - O$$

Also,

$$R-C-OH+CH_2N_2 \longrightarrow O$$
 $\parallel R-C-O^-+CH_2-N^+ \equiv N$

$$R - \stackrel{\bigcirc{C}}{C} - \stackrel{\bigcirc{C}}{O} + \stackrel{\frown{C}}{C} \stackrel{+}{H_3} \stackrel{-}{N} = N \xrightarrow{-N_2} \stackrel{-}{\underset{R-C-O-CH_3}{\longrightarrow}}$$

One well-known yet important concept may be revisited.

Without going details into the mechanism just note alcohol is showing acidity in such esterification.

Important usages.

- Formic acid is used in the leather industry to remove hair from hides and as an ingredient in tanning formulations. It is used as latex coagulant in natural rubber production.
- Formic acid reduces clostridia bacteria that helps preserving protein and sugar content and is thus used as food preservative.

- O Formic acid is used as a miticide by beekeepers.
- Sodium formate and potassium formate are used as deicing agent for airport runways and roads.
 Formates are used as brightening agents in textiles.
 Formates are also used in wood preservatives, resins, plasticizers, perfume fragrances, etc.
- O Acetic acid is used in the manufacture of a wide variety of products including adhesives, polyester fibres, plastics, paints. A large percentage of acetic acid is used in the manufacture of vinyl acetate monomer for the plastics industry. Vinegar, a dilute solution of acetic acid in water, has been a vital ingredient of foodstuffs.
- Decarboxylation of β-keto acids is easier that takes place at even 25°C.

$$H_3C'$$
 C
 OH
 H_3O^*
 H_3C'
 C
 CH_3

 β-diacids also undergo decarboxylation but at a higher temperature.

$$\begin{array}{c} \xrightarrow{\text{COOH}} \xrightarrow{185^{\circ}\text{C}} & \xrightarrow{\text{H}} & \xrightarrow{\text{COOH}} & \\ \xrightarrow{\text{COOH}} & \xrightarrow{185^{\circ}\text{C}} & \xrightarrow{\text{COOH}} & \xrightarrow{\text{COOH}} & \\ \end{array}$$

O₂N-CH₂-COOH, NC-CH₂-COOH,

R—CH=CH—CH₂—COOH also undergo decarboxylation.

 Acid derivatives like acyl chloride and ester preparation methods involve very simple reactions, like treating a carboxylic acid with PCl₅, PCl₅, SOCl₂, alcohol, etc. Let's note few other important reactions.

$$CH_3 - C - CH_3 \xrightarrow{750^{\circ}C} CH_2 = C = O + CH_4$$
or,

$$CH_3 - C - OH \xrightarrow{750^{\circ}C} CH_2 = C = O + H_2O$$

 Ketene is now treated with acetic acid to get acid anhydride or alcohol to get ester. On treatment with ammonia it gives amide.

$$\begin{array}{c} \text{CH}_3\text{-OH} \\ \text{CH}_2\text{=C=O} \\ \text{CH}_3\text{-CO} \\ \text{CH}_3\text{-CO} \\ \text{CH}_3\text{-CO} \\ \text{CH}_3\text{-CO} \\ \text{CH}_3\text{-CO} \\ \text{NH}_3 \\ \text{CH}_3\text{-CO} \\ \text{NH}_2 \\ \end{array}$$

While preparing acid derivatives starting from another acid derivative using simple nucleophiles like CT, ROH, NH₃, RCOOH note that the conversion is possible only downhill of the given arrangement.

Acyl chloride
Acid anhydride
Ester
Amide

$$R = C - OR - CI^-$$
No acyl chloride

 $R = C - CI - NH_3$
 $R = C - CI - NH_2$
 $R = C - CI - R - ROH$
 $R = C - CI - ROH$

 All the derivatives of acids can be forced to react with water to regenerate the parent acid. The reactivity towards water decreases as

The famous Arndt-Eistert synthesis involves a

$$R-CH_2-C-OH \xrightarrow{2. CH_2N_2} \xrightarrow{3. Ag_2O/A} \xrightarrow{0} \xrightarrow{1.4 + 120} = R-CH_2-C-OH$$

Just after heating with Ag_2O , we were having $R - CH_2 - CH = C = O$, which is attacked by H_2O , a nucleophile.

$$H_2O$$
, a nucleophile.
 $R-CH_2-\overrightarrow{CH}=\overrightarrow{C}-O\rightarrow R-CH_2-CH_2-\overrightarrow{C}-OH$
 \overrightarrow{O}

Hydrolysis of acyl chlorides and anhydrides do not require even catalysis.

Both esters and amides are hydrolysed in acidic as well as alkaline medium. Remember basic hydrolysis of amide is even easier than acidic hydrolysis.

Here comes reduction reactions

$$R - C - OR' \xrightarrow{1. \text{ LiAlH}_4} R - CH_2OH + R'OH$$

Alternatively, Na/alcohol or H2 in presence of CuCr2O4 at 175°C under high pressure may be

$$R - C - OR' \xrightarrow{\text{Na metal in the absence}} R - C - CR' \xrightarrow{\text{Na metal in the absence}} R - C - C - R \xrightarrow{\text{OH O}} H_2O$$

$$R - C - C - R \leftarrow H_2O$$

$$R - C - C - R \leftarrow H_2O$$

$$R - C - C - R \leftarrow H_2O$$

$$R-C \stackrel{\text{i. c.i.d.i.4.}}{\bigcirc O} + R-CH_2-OH$$

$$R-C \stackrel{\text{i. c.i.d.i.4.}}{\bigcirc O} + R-CH_2-OH$$

$$- H_2 \qquad \qquad O$$

$$- H_2 \qquad \qquad |I|$$

$$- Pd-BaSO_4 \rightarrow R-C-H$$

$$0$$

$$0$$

$$1. LiAl(O-I-Bu)_3H \qquad |I|$$

$$2. H_0/H^2 \rightarrow R-C-H$$

Again,

$$R - \overset{\text{O}}{\text{C}} - \text{NH}_2 \xrightarrow{\text{1. LiAlH}_4} R - \text{CH}_2 - \text{NH}_2$$

Reactions with organic metallic reagents are always important.

$$OC_{2}H_{5} \xrightarrow{1. \text{ PhMgBr } (2 \text{ moles})} OC_{2}H_{5} \xrightarrow{1. \text{ PhMgBr } (2 \text{ moles})} OC_{2}H_{5}$$

but

$$\bigcap_{R} \bigcup_{NH_2} \bigcap_{R'MgX} \bigcap_{R} \bigcup_{NHMgX+R'H} \bigcap_{NHMgX+R'H} \bigcap_{R'MgX+R'H} \bigcap_{R'MgX+R'$$

The above reaction is an acid-base reaction. Grignard reagent sees amide as an acid! Slight modification gives different result.

$$\bigcap_{\substack{I \subseteq CH_3 \\ CH_3}} CH_3 + R' - MgX \longrightarrow R - \bigcap_{\substack{I \subseteq C-N \\ R'}} CH_3$$
Stable until acidified
$$\bigcap_{\substack{I \subseteq CR' \\ R-C-R' \\$$

See another interesting reaction.

attacked by nucleophile)

$$\stackrel{\bar{\operatorname{OLi}}}{\triangleright} \stackrel{\circ}{\underset{C}{\operatorname{CH}_3}} \stackrel{\circ}{\underset{CH_3}{\operatorname{H}^*}} \stackrel{\circ}{\underset{CH_3}{\operatorname{H}_3}} \stackrel{\circ}{\underset{CH_3}{\operatorname{H}_3}}$$

Dialkyl cadmium is a soft nucleophile. Acyl chloride reacts with dialkyl cadmium to give ketone, which is not further attacked by nucleophile dialkyl cadmium.

$$\begin{array}{ccc}
O & O \\
R - C - CI & \xrightarrow{R'_2 Cd} & R - C - R'
\end{array}$$

 Hunsdiecker reaction is another decarboxylation reaction. It involves heating a Ag-salt of carboxylic acid with Br2 in dry CCl4.

$$\begin{array}{c}
O \\
R - C - \bar{O}Ag^* + Br_2 \xrightarrow{Dry} \begin{bmatrix}
O \\
R - C - O - Br
\end{bmatrix}$$

$$R - Br + CO_2 \longleftarrow$$

Alternatively, the same reaction can be affected by heating the acid and bromine with HgO. The reaction involves free radical.

Reactivity of carboxylic acids at the α-position is illustrated by HVZ reaction.

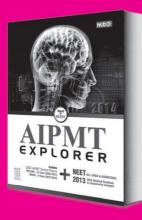
$$R-CH_{2}-C \xrightarrow[OH]{P} R-CH-C \xrightarrow[Br]{O} \xrightarrow{H_{2}O}$$

$$R-CH-C \xrightarrow{OH} R-CH-C \xrightarrow{OH} R$$

No need to check the mechanism. Another way to illustrate the reactivity of α-position is to use LDA (Lithium Di-isopropyl Amide).

$$R-CH_{2}-COH \xrightarrow{LDA} R-CH_{2}-COH \xrightarrow{LDA} R-CH_{2}-COH \xrightarrow{R-CH-COH} R-CH-COH \xrightarrow{R-1} R-CH-CH-COH \xrightarrow{R-1} R-CH-CH-COH \xrightarrow{R-1} R-CH-CH-COH \xrightarrow{R-1} R-CH-CH-COH \xrightarrow{R-1} R-CH-CH-COH \xrightarrow{R$$

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Recall that LDA *i.e.* Lithium Di-isopropyl Amide is a strong and bulky base.

Claisen and Dieckmann condensation reactions are observed on esters.

$$R$$
-CH₂-C+ OR' +H+CH-C- OR'

$$\begin{array}{c}
1. R'\bar{O}Na^* \text{ (excess)} \\
2. H^*
\end{array}$$

$$R-CH_2-C-CH-C-OR$$

Without analysing the mechanism based explanation just remember:

- The alkoxy group of ester and the alkoxide must carry the same alkyl group. Alkoxide should be used in excess.
- There must be at least two α-hydrogens in ester.
- The intramolecular Claisen condensation is known as Dieckmann condensation.

$$\begin{array}{c} O \\ O \\ O \\ O \\ O \end{array}$$

$$\begin{array}{c} O \\ O \\ O \\ O \end{array}$$

$$\begin{array}{c} O \\ O \\ O \\ O \end{array}$$

 Active methylene compounds like diethyl malonate can be used to synthesise many compounds. Consider an example diethyl malonate.

$$\begin{array}{c} O \\ | \\ C \\ -OC_2H_5 \\ | \\ C \\ -OC_2H_5 \\ | \\ | \\ O \end{array} \xrightarrow{C_2H_5O^*N_4^*} \begin{array}{c} O \\ | \\ C \\ -OC_2H_5 \\ | \\ | \\ O \\ O \end{array}$$

$$R \xrightarrow{R-Br} R \xrightarrow{C} CH \xrightarrow{C-OC_2H_5} \xrightarrow{H_5O^*} R \xrightarrow{C} C-OH$$

$$\downarrow C \xrightarrow{C} CC_2H_5 \xrightarrow{H_5O^*} R \xrightarrow{C} C-OH$$

$$\downarrow C \xrightarrow{C} COH$$

$$\downarrow C \xrightarrow{C} COH$$

$$\downarrow C \xrightarrow{C} COH$$

 Now its time to see some conjugate addition. In such reactions the C=C bond in conjugation to -COOH or -COOR give nucleophilic addition.

$$CH_2=CH-\overset{\square}{C}-OH \xrightarrow{HCl} CH_2=CH\overset{\square}{C}-OH$$

$$OH \qquad 0$$

$$OH \qquad 0$$

$$CH_2-CH=C-OH \rightleftharpoons CH_2-CH_2-C-OH$$

$$Cl \qquad Cl \qquad Cl$$

Some more examples are

$$\begin{array}{c} \xrightarrow{R_2\mathrm{NH}} R_2\mathrm{N-CH}_2\mathrm{-CH}_2\mathrm{-C} \\ \xrightarrow{\mathrm{CH}_2=\mathrm{CH-C}} & \xrightarrow{\mathrm{HOH}} & \mathrm{CH}_2\mathrm{-CH}_2\mathrm{-C} \\ \xrightarrow{\mathrm{OR}} & \xrightarrow{\mathrm{NC}} & \mathrm{NC-CH}_2\mathrm{-CH}_2\mathrm{-C} \\ \xrightarrow{\mathrm{C}_{2\mathrm{H_3OH}}} & \mathrm{NC-CH}_2\mathrm{-CH}_2\mathrm{-C} \\ \xrightarrow{\mathrm{C}_{2\mathrm{H_3OH}}} & \mathrm{NC} \end{array}$$

 γ , δ -unsaturated acids react with strong acids to give lactones.

$$CH_2 = CH - CH_2 - CH_2 - CH_2 - CH_3 - CH_2 - CH_2 - CH_2 - CH_3 - CH$$

Important usages.

 Acetic anhydride is used in the manufacture of cellulose acetate for photographic films.
 A little percentage of the entire production is used for aspirin synthesis. Other usages include the manufacture of industrial chemicals, pharmaceuticals, perfumes, weed killers.

It is also a restricted chemical in many countries as it is used clandestinely for the purification of banned drugs.

Acetyl chloride is largely used as an acetylating agent i.e. as a means of introducing the acetyl group, into compounds containing active hydrogen atoms. It is also used to detect the presence of hydroxyl groups in organic compounds.

Before we close see some important reactions from examination point of view.





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$$R - C - NH_2 \xrightarrow{P_2O_5/\Delta}_{\text{or, SOCly/benzene}} R - C \equiv N$$

$$\begin{array}{c}
\text{COOH} \\
\text{COOH}
\end{array}$$

$$\begin{array}{c} 2R-\text{CH-COOH} \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} 0 \\ C \\ C \\ R \end{array}$$

$$\begin{array}{c|c} CH_3 & CH_3 \\ CH_3 - C - CH_3 + HCOOH \\ CH_3 & OH \end{array} \xrightarrow{98\% \ H_2SO_4}$$

ÓН

$$CH_2 = CH_2 \xrightarrow{H^+} CH_3 - CH_2 - \overset{+}{C} = O \xrightarrow{H_2O}$$
 $CH_3 - CH_2 - \overset{-}{C} = O$

Coming to boiling points

$$O = \bigcup_{\substack{\text{H}_{3}C\\\text{b.pt.} 221.2^{\circ}C}} \bigcup_{\substack{\text{H}_{2}C\\\text{b.pt.} 204^{\circ}C}} \bigcup_{\substack{\text{NH}-\text{CH}_{3}\\\text{b.pt.} 166.1^{\circ}C}} \bigcup_{\substack{\text{CH}_{3}\\\text{b.pt.} 166.1^{\circ}C}} CH_{3}$$

Finally, see why formic acid is called as polar solvent but not acetic acid.

$$\begin{array}{c} O \\ C \\ CH_3-C-OH \\ Acetic acid \\ \mu = 1.5 - 1.7 \ D \\ Dielectric constant \\ = 6.1 \\ \end{array}$$
 $\begin{array}{c} O \\ H-C-OH \\ Formic acid \\ \mu = 1.6 - 1.8 \ D \\ Dielectric constant \\ Dielectric constant \\ = 50 \\ \end{array}$

Did you check, it is not the dipole moment but the dielectric constant that gives the name 'polar' to a solvent.

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CHEMISTRY MUSING

SOLUTION SET 6

 (b): According to the Arrhenius equation $k = Ae^{-E_a/RT}$

Let the activation energy (E_a) in the absence of

catalyst = x kI mol⁻¹. Then the activation energy in the presence of catalyst will be (x - 20) kJ mol⁻¹

At 580 K;
$$k = Ae^{-x/580 R}$$
 ...(i)
At 420 K; $k = Ae^{-(x-20)/420 R}$...(ii)

Divide (i) by (ii), we get

$$1 = \frac{e^{-x/580R}}{e^{-(x-20)/420R}} \implies e^{-(x-20)/420R} = e^{-x/580}$$
$$\frac{-(x-20)}{420R} = \frac{-x}{580R}$$

By solving above equation we get, $x = 72.5 \text{ kJ mol}^{-1}$

2. (a) : Al₂O₃ + 3C + N₂ → 2AlN + 3CO 1 mole of Al2O3 requires 3 moles of carbon i.e., 102 g of Al₂O₃ requires 3 × 12 g of carbon

So, 23 g of Al₂O₃ requires
$$\frac{3\times12}{102}\times23$$

= 8.12 g of carbon

(c) : Claisen condensation

$$\begin{array}{c} \text{2CH}_3\text{CO}_2\text{C}_2\text{H}_5 & \frac{\text{C}_2\text{H}_5\text{ONa}}{\text{C}_2\text{H}_5\text{OH}} \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H} \\ \text{CH}_2 = \text{C} & \text{heated in presence of } \\ \text{on} & \text{acid (H')} \end{array}$$

Mechanism:

$$\begin{array}{c} \text{CH}_{3} - \text{C} - \text{C} - \text{C} - \text{OC}_{2} \text{H}_{5} \xrightarrow{\text{heat}} \text{CH}_{2} - \text{C} - \text{C} + \text{E} \xrightarrow{\text{C}} \text{C} \\ \text{H} \\ \text{(P)} \\ \text{CH}_{2} = \text{C} \xrightarrow{\text{CH}_{2}} \text{C} = \text{O} \end{array}$$

- 4. (c): The compound is said to be chiral if the central atom is attached to four different groups and the molecule has no plane of symmetry.
- 5. (d): $3SCl_2 + 4NaF \xrightarrow{70-90^{\circ}C} SF_4 + S_2Cl_2 + 4NaCl$
- (d): 1, 4-Pentadiene reacts with HCl, in presence of peroxide, in accordance with Markovnikov's rule.

Grignard's reagent on reaction with ethyl acetate forms ketone or tert. alcohol if we use excess of Grignard's reagent.

Grignard's reagent.
Reactions:

$$H_2C = CH - CH_2 - CH = CH_2 \frac{HCl}{peroxide}$$
 M_g . M_g

As $M - 2e^- \longrightarrow M^{2+}$ Thus, n = 2

 $\Delta G = -2 \times 0.059 \times 96500 = -11.387 \text{ J/mol} = -11.4 \text{ kJ/mol}$

(b): For concentration cell.

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2(\text{RHS})}}{C_{1(\text{LHS})}}$$

 $E_{\text{cell}} = 0.059 \text{ V}, C_{2(\text{RHS})} = 0.001 \text{ M}$

$$\begin{array}{l} 0.059 = \frac{0.0591}{2} \log \frac{0.001}{C_1} \implies \frac{2 \times 0.059}{0.0591} = \log \frac{0.001}{C_1} \\ \implies \text{ antilog } 2 = \frac{0.001}{C_1} \implies C_1 = \frac{0.001}{100} = 10^{-5} \end{array}$$

 C_1 = Concentration or solubility of M^{2+} = 10^{-5}

$$MX_2 \Longrightarrow M^{2+} + 2X^-$$

 $S = 2S$

$$MX_2 \rightleftharpoons M^{2+} + 2X^{-}$$

 $S = 2S$
 $K_{sp} = S(2S)^2 = 4S^3$
 $K_{sp} = 4 \times (10^{-5})^3 = 4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$

- 9. (4): SF_{64} XeO_2F_{44} BrF_5 and IF_5 have sp^3d^2 hybridisation in their geometrical structures.
- (6): Fe²⁺ is oxidised to Fe³⁺ and C₂O₄²⁻ is oxidised to CO2 by MnO4 in acidic medium.

$$\begin{array}{c} 5Fe^{2+} + MnO_4^- *8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \\ 5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} \\ + 8H_2O \end{array}$$

$$5 \text{FeC}_2 \text{O}_4 + 3 \text{MnO}_4^- + 24 \text{H}^+ \longrightarrow 5 \text{Fe}^{3+} + 10 \text{CO}_2 + 3 \text{Mn}^{2+} + 12 \text{H}_2 \text{O}$$

Thus, 5 moles of $\text{FeC}_2 \text{O}_4$ are oxidised by 3 moles

1.44 g (*i.e.*,
$$\frac{1.44}{144}$$
 = 0.01 mol) FeC₂O₄ is oxidised by = $\frac{3}{5} \times 0.01$ = 0.006 mol of MnO₄

If V mL of 0.01 M KMnO4 are required then

$$\frac{0.01 \times V}{1000} = 0.006$$
 (: No. of moles = $\frac{MV}{1000}$)

∴ V = 600 mL

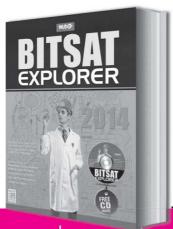
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ESSENTIAL REACTIONS

FOR COMPETITIVE EXAMS

REDOX REACTIONS

Redox reaction (Oxidation-reduction)



Types of redox reactions:

- Combination reaction

$$0 0 \Delta \Rightarrow 12 -3$$

 $3Mg + N_2 \Delta \Rightarrow Mg_3N_2$

- Decomposition reaction $^{+1}$ $^{+5-2}$ $^{-2}$ $^{+1-1}$ $^{-1}$ 0 2 2 2 2 2 2 2 2 2 2
- Displacement reaction
- (a) Metal displacement

(b) Non-metal displacement

$${}^{0}_{2\text{Fe}} + {}^{+1}_{3} + {}^{-2}_{2} \longrightarrow {}^{+3}_{7} + {}^{-2}_{3} + {}^{3}_{3} + {}^{2}_{3}$$

- Disproportionation reaction

$$^{+1}_{2H_2O_2} \xrightarrow{+1} ^{-2}_{2H_2O} \xrightarrow{+O_2}$$

- In C₃O₂, oxidation number of carbon is 4/3.
- In Br₃O₈, oxidation number of bromine is 16/3.
- In Na₂S₄O₆, oxidation number of sulphur is 2.5.
 The element having fractional oxidation state is
- The element having fractional oxidation state is realised to present in different oxidation states.

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} -2 = C & = 2 \\ O = C = C = C = C \\ O = C \\ O$$

 In redox systems, the titration method can be adopted to determine the strength of a reductant/ oxidant using a redox sensitive indicator.



- MnO₄ acts as the self-indicator.
- Cr₂O₇², which is not a self-indicator but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour thus signalling the end point.
- Iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions (\$\gamma_0^2\gamma^2\gm), which is a redox reaction.
- $2Cu^{2+} + 4I^{-} \rightarrow Cu_{2}I_{2} + I_{2}$
- $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

HYDROGEN

- The first element in the periodic table.
 - Electronic configuration: 1s1
- Three isotopes: protium, ¹₁H, deuterium, ²₁H or D and tritium, ³₁H or T.
- Laboratory preparation

$$Zn + H_2SO_4(dil.) \rightarrow ZnSO_4 + H_2\uparrow;$$

 $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$

Commercial production

$$2H_2O \xrightarrow{\text{Electrolysis}} 2H_2 + O_2$$

$$2Na^+ + 2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2Na^+ + 2OH^-$$
At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
At cathode: $2H_3O + 2e^- \rightarrow H_2 + 2OH^-$

•
$$C_nH_{2n+2} + nH_2O \xrightarrow{1270 \text{ K}} nCO + (2n+1)H_2$$

 The process of producing 'syngas' from coal is called 'coal gasification'.

$$C + H_2O \xrightarrow{1270 \text{ K}} CO + H_2$$

• CO + H₂O $\xrightarrow{673 \text{ K}}$ CO₂ + H₂

This is called water-gas shift reaction.

Chemical properties
 H₂ + X₂ → 2HX; (X = F, Cl, Br or I)

$$2H_2 + O_2 \xrightarrow{\text{catalyst/heating}} 2H_2O$$

$$3H_2 + N_2 \xrightarrow{\text{673 K,200 atm}} 2NH_3$$

 $H_2 + 2M \rightarrow 2MH$; where M is an alkali metal.
$$\begin{split} &H_2 + Pd^{2+} \rightarrow Pd + 2H^+ \\ &yH_2 + M_4O_y \rightarrow xM + yH_2O \\ &H_2 + CO + RCH == CH_2 \rightarrow RCH_2CH_2CHO \\ &H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2CH_2OH \end{split}$$

Chemical properties of water

 $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(Self-ionization of water)

 $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^$ acid base acid base

(Amphoteric character)

$$2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2$$

(As an oxidizing agent)

$$2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$$

$$nCO_2 + nH_2O \xrightarrow{\text{Sunlight}} Chlorophyll} (CH_2O)_n + nO_2$$
Carbohydrate

(As a reducing agent)

 Water is said to be soft if it produces sufficient lather with soap while it is said to be hard if it forms an insoluble scum before it forms lather with soap.

$$2C_{17}H_{35}COONa + M^{2+} \rightarrow (C_{17}H_{35}COO)_2 M \downarrow + 2Na^+;$$

(M is Ca/Mg)

- Removal of temporary hardness:
 - (a) Boiling: $Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$ $Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$
 - (b) Clark's process: $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow$ $+ 2H_2O$ $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow$ $+ Mg(OH)_3 \downarrow + 2H_3O$
- Removal of permanent hardness: $MCl_2+Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl \ (M = Mg, Ca)$ $MSO_4+Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$ $MsO_6+Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$ $Ma_6P_6O_{18} \rightarrow 2Na^* + Na_4P_6O_{18}^2 \ (M = Mg, Ca)$ $M^{2+}+Na_4P_6O_{18}^2 \rightarrow (Na_2MP_4O_{18})^{2-} + 2Na^*$ $2NaZ + M^{2+} \rightarrow MZ_2 + 2Na^* \ (M = Mg, Ca)$ $MZ_2 + 2NaCl \rightarrow 2NaZ + MCl_2$ $2RNa + M^{2-} \rightarrow R_2M + 2Na^*$ $2RH + M^{2+} \rightarrow MZ_2 + 2H^*$ $RNH_2 + H_2O \Rightarrow RNH_3^*, OH^-$
- $RNH_3^+OH^- + X^- \rightleftharpoons RNH_3^+, X^- + OH^-$ Hydrogen peroxide
 Preparation $BaO.8H_3O + H_3SO_4 \rightarrow BaSO_4 + H_3O_7 + 8H_3O_7$

2HSO₄
$$\xrightarrow{\text{Electrolysis}}$$
 HO₃SOOSO₃H $\xrightarrow{\text{Hydrolysis}}$ 2HSO₇ + 2H⁺ + H₂O₂

 $K_2S_2O_8 + 2D_2O \rightarrow 2KDSO_4 + D_2O_2$ 2-ethylanthraquinol $\xrightarrow{O_2(air)}$ $H_2O_2 +$

oxidised product

- Chemical properties
- Oxidising action in acidic medium 2Fe²⁺ + 2H⁺ + H₂O₂ → 2Fe³⁺ + 2H₂O PbS + 4H₂O₂ → PbSO₄ + 4H₂O
- Reducing action in acidic medium
 2MnO₄⁻ + 6H⁺ + 5H₂O₂ → 2Mn²⁺ + 8H₂O + 5O₂
 HOCl + H₂O₂ → H₃O⁺ + Cl⁻ + O₂
- Oxidising action in basic medium $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^ 4Fe^{2+} + H_3O_2 \rightarrow Mn^{4+} + 2OH^-$
- Reducing action in basic medium $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$ $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$
- Heavy water, D₂O
 CaC₂+2D₂O → C₂D₂+Ca(OD)₂
 SO₃+D₂O → D₂SO₄
 Al₄C₃+12D₂O → 3CD₄+4Al(OD)₃

THE s-BLOCK ELEMENTS

- Alkali metals : [noble gas]ns1
- Alkaline earth metals : [noble gas]ns2
- Chemical properties of alkali metals 4Li + O₂ → 2Li₂O (Oxide)

4-11 + O_2 → 2.1-12 (Oxhde) $M + O_2$ → Na_2O_2 (Peroxide) $M + O_2$ → MO_2 (Superoxide) (where, M = K, Rb, Cs) $2M + 2H_2O \rightarrow 2M^* + 2OH^- + H_2$ [M = an alkali metal] $2M + H_2$ $\xrightarrow{\Delta}$ 2 M^*H^-

 $2M + X_2 \rightarrow 2M^+X^-$

 $M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$

ammoniated cation causes conductivity electron responsible for blue colour and

paramagnetism

 $M_2O + H_2O \rightarrow 2M^+ + 2OH^ M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$ $2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$ $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ $2NaNO_3 \rightarrow 2NaNO_3 + O_3$

Some important reactions
 2NH₃ + H₂O + CO₂ → (NH₄)₂CO₃
 (NH₄)₂CO₃ + H₂O + CO₂ → 2NH₄HCO₃
 NH₄HCO₃ + NaCl → NH₄Cl + NaHCO₃

BEST TOOLS FOR SUCCESS IN

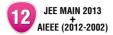
JEE Main











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$$\begin{split} 2\text{NaHCO}_3 &\rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \\ 2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 &\rightarrow 2\text{NH}_3 + \text{CaCl}_2 + 2\text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \xrightarrow{375\text{ K}} &\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 9\text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} \xrightarrow{>373\text{ K}} &\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\ \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{NaHCO}_3 \end{split}$$

• Chemical properties of alkaline earth metals $M + X_2 \rightarrow MX_2$ (X = F, Cl, Br, I)

BeO + C + Cl₂
$$\xrightarrow{600-800 \text{ K}}$$
 BeCl₂ + CO
2BeCl₂ + LiAlH₄ \rightarrow 2BeH₂ + LiCl + AlCl₃
 M + 2HCl \rightarrow M Cl₂ + H₂
 M + $(x + y)$ NH₃ \rightarrow $[M(NH_3)_x]^{2^x}$ + 2 $[e(NH_3)_y]^T$
 MO + H₂O \rightarrow $M(OH)_2$
Be(OH)₂ + 2OH⁻ \rightarrow $[Be(OH)_4]^2$
Beryllate ion
Be(OH)₂ + 2HCl \rightarrow BeCl₂ + 2H₃O

$$2M(NO_3)_2 + 2MO + 4NO_2 + O_2$$

$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

[M = Be, Mg, Ca, Sr, Ba)

Important reactions

$$\begin{array}{c} \text{CaCO}_3 & \xrightarrow{\text{heat}} & \text{CaO} + \text{CO}_2 \\ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 \\ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \\ \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \\ \text{6CaO} + \text{P}_4\text{O}_{10} \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 \\ \text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \\ \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2 \\ \end{array}$$

 $2\text{Ca}(\text{OH})_2 + 2\text{Cl}_2 \rightarrow \text{Ca}(\text{Cl}_2 + \text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{O}$ Bleaching powder

 $\begin{array}{c} CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl \\ CaCO_3 \xrightarrow{1200 \text{ K}} CaO + CO_2 \end{array}$

 $CaCO_3 + 2HCI \rightarrow CaCI_2 + H_2O + CO_2$ $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$ $2(CaSO_4 \cdot 2H_2O) \rightarrow 2(CaSO_4) \cdot H_3O + 3H_3O$

THE p-BLOCK ELEMENTS

- Electronic configuration : ns²np¹⁻⁶ (except for He)
- Chemical properties

$$\begin{array}{c} 4E + 3O_2 \stackrel{\Delta}{\longrightarrow} 2E_2O_3 \\ 2E + N_2 \stackrel{\Delta}{\longrightarrow} 2EN \\ 2AI + 6HCI \rightarrow 2AI^{3+} + 6CI^- + 3H_2 \\ 2AI + 2NaOH + 6H_2O \rightarrow 2Na'[AI(OH)_4]^- + 3H_2 \\ Sodium \end{array}$$

tetrahydroxoaluminate(III) $2E + 3X_2 \rightarrow 2EX_3$ (X = F, CI, Br, I) $F_3B + :NH_3 \longrightarrow F_3B \leftarrow NH_3$ $Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$

Orthoboric acid

$$Na_{2}B_{4}O_{7}-10H_{2}O \xrightarrow{\Delta} Na_{2}B_{4}O_{7} \xrightarrow{\Delta} 2NaBO_{2} \\ Sodium \\ metaborate & Boric \\ anhydride \\ Na_{2}B_{4}O_{7}+2HCl+5H_{2}O \rightarrow 2NaCl+4B(OH)_{3} \\ B(OH)_{3}+2HOH \rightarrow [B(OH)_{4}]^{+}+H_{5}O^{+} \\ H_{5}BO_{3}\xrightarrow{\Delta} +BBO_{2}\xrightarrow{\Delta} B_{2}O_{3} \\ 4BF_{3}+3LiAlH_{4}\rightarrow 2B_{2}H_{6}+3LiF+3AlF_{3} \\ 2NaBH_{4}+I_{2}\rightarrow B_{2}H_{6}+2NaI+H_{2} \\ 2BF_{3}+6NaH \xrightarrow{450K} B_{2}H_{6}+6NaF \\ B_{2}H_{6}+3O_{2}\rightarrow B_{2}O_{3}+3H_{2}O \\ B_{3}H_{6}+6H_{2}O\rightarrow 2B(OH)_{3}+6H_{2} \\ B_{4}H_{6}+2CO\rightarrow 2BH_{3}\cdot CO \\ 3B_{2}H_{6}+2CO\rightarrow 2BH_{3}\cdot CO \\ 3B_{2}H_{6}+6NH_{3}\rightarrow 3[BH_{2}(NH_{3})_{2}]^{+}[BH_{4}]^{-} \xrightarrow{Heat} \\ 2B_{3}N_{3}H_{6}+12H_{2} \\ Borazine \\ (Inorganic benzene) \\ 2MH+B_{2}H_{6}\rightarrow 2M^{+}[BH_{4}]^{-} (M=Li \ or \ Na) \\ Sin+2H_{2}O\xrightarrow{4}SnO_{2}+2H_{2} \\ SiCl_{4}+4H_{2}O\xrightarrow{-4HCl}Si(OH)_{4} \\ Sillicic acid \\ 1mportant reactions \\ 2C+O_{2}\xrightarrow{\Delta}2CO \\ HCOOH\xrightarrow{473-1273K} CO+H_{2} \\ Water gas \\ 2C+O_{2}+4N_{2}\xrightarrow{-1273K}2CO+4N_{2} \\ Producer gas \\ 3CO+Fe_{2}O_{3}\xrightarrow{\Delta}2Fe+3CO_{2} \\ CO+ZnO\xrightarrow{\Delta}Zn+CO_{2} \\ SiO_{2}+2NaOH\rightarrow Na_{2}SiO_{3}+H_{2}O \\ SiO_{2}+2NaOH\rightarrow Na_{2}SiO_{3}+H_{2}O \\ SiO_{2}+4HF\rightarrow SiF_{4}+2H_{2}O \\ 2CH_{3}Cl+Si\xrightarrow{CH_{3}OHP}(CH_{3})_{2}SiCl_{2} \\ (CH_{3})_{2}Si(OH)_{2}\xrightarrow{-12HCl} \\ CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} \\ -H_{2}O Polymerisation \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} \\ -O\xrightarrow{CH_{3}OHP}(CH_{3})_{n}CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3}$$

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